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# HIGH-VALUE MULTILAYER GRAPHENE OXIDE PREPARED BY CATALYTIC PYROLYSIS OF PETROLEUM TAR AND APPLICATIONS: TRASH TO TREASURE

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#### ABSTRACT

Petroleum tar (PT), a by-product of heavy oil refining, poses significant environmental challenges due to its high production volume and associated pollution risks. This study presents an innovative approach for the catalytic conversion of PT into multilayer graphene oxide using nickel foam (NiF) as a catalyst at reaction temperatures of 500°C and 700 °C (GT/Ni500 and GT/Ni700). The process effectively decomposes PT and facilitates the structured rearrangement of carbon atoms into graphene layers. Comprehensive characterization techniques, including SEM-EDS, HRTEM, BET, XRD, XPS, and Raman spectroscopy, confirm the formation of high-quality graphene oxide. GT/Ni700 material The synthesized exhibits remarkable electrochemical performance with a specific capacitance of 3.34 F/g. GT/Ni500 shows adsorption capacities of 59.86 mg/g for Pb2+ and 56.84 mg/g for Cu<sup>2+</sup>. Life Cycle Assessment reveals a substantial reduction in the carbon footprint, with CO2 equivalents for GT/Ni500 and GT/Ni700significantly lower than traditional methods, at 17.64 kg/CO2eq and 14.03 kg/CO2eq, respectively, representing a reduction of over 50%. This study not only offers a sustainable pathway for PT utilization but also provides advanced materials with dual utility in electrochemical applications and heavy metal adsorption, contributing to environmental remediation and reducing reliance on non-renewable resources.

### **RESULTS AND DISCUSSION**

Liquid and gas phase products

Figure 1a shows the original PT composition and PT conversion efficiency, along with pyrolysis oil composition at 700 °C without a catalyst, and at 500 °C and 700 °C with NiF as a catalyst. Initially, PT primarily consists of polycyclic aromatic hydrocarbons (PAHs), making up 92.08%, which remain stable and difficult to break during pyrolysis. Without a catalyst,

PT conversion is 47.74%, with PAHs still dominating the residual tar. Using NiF at 500 °C, the conversion improves to 72.14%, with 9,9-Dimethylfluorene becoming the main tar component. The three-ring aromatic compounds reduce from 42.30% to 22.00%, indicating catalytic activity. At 700 °C, NiF increases the conversion rate to 85.50%, highlighting a 79.10% improvement over non-catalytic conditions. Mono-aromatic hydrocarbons, mainly 1-Phenyl-1-propyne, dominate the residual tar, suggesting NiF effectively breaks down PAHs into simpler mono-aromatics, beneficial for further chemical processing and with higher market value. Figure 1b illustrates gas component changes during PT pyrolysis. NiF catalysis increases H2 and CO, while reducing CO2 content. The thermal energy of non-catalytic PT gas is 6.89 kWh/kg, which rises to 7.35 kWh/kg at 700 °C under NiF, indicating efficient energy recovery. The increase in  $\mathrm{H_2}$  and  $\mathrm{CO}$  production at 700 °C results from the breakdown and rearrangement of aromatic structures, releasing more combustible gases. Thus, NiF-catalyzed pyrolysis enhances PT conversion, optimizes gas yield, and improves energy efficiency.



Figure 1 Liquid phase (a) and gas phase (b) product components after catalytic pyrolysis.

### **Material Characterization Analysis**

SEM analysis shows GT/Ni has a 3D network structure, derived from NiF, without cracks (Figure 2). EDS indicates a uniform carbon coating on nickel foam, with minimal Ni presence. The pore volume of GT/Ni500 is

 $0.0010 \text{ cm}^3/\text{g}$  and a pore size of 3.86 nm, suggesting medium-sized pores. GT/Ni700 shows a larger specific surface area (1.25 m²/g) and pore size (4.18 nm), indicating improved charge storage and ion adsorption capacity. SEM and BET analyses suggest the structure's origin is from NiF, and GT/Ni700's larger surface area may be due to lower carbon content.



Figure 2 (a) and (d): SEM images showing the porous structures and elemental composition of the GT/Ni500 and GT/Ni700 samples, respectively; (b) and (e): High-magnification SEM images illustrating the pore structure of GT/Ni500 and GT/Ni700, with corresponding BET surface area, pore volume, and pore size.

HRTEM and SAED confirm that both GT/Ni500 and GT/Ni700 have multilayer graphene oxide structures, with GT/Ni700 showing monolayer graphene edges (Figure 3). The SAED pattern of GT/Ni700 reveals a hexagonal single-crystal structure. Lattice fringes are clear for both materials, consistent with Ni's (100) lattice.



Figure 3 (a) and (d): HRTEM images of GT/Ni500 and GT/Ni700, with the insets displaying the corresponding SAED patterns; (b, c) and (e, f): Higher magnification HRTEM images of GT/Ni500 and GT/Ni700.

XRD spectra confirm Ni encapsulation within GT/Ni, which serves as a catalyst and current collector, enhancing energy recovery and enabling magnetic separation. A peak at 13.95° for GT/Ni700 indicates an increase in interlayer spacing, suggesting graphitization. FTIR analysis (Figure 4b) shows that GT/Ni retains certain functional groups from PT and introduces new ones. Peaks at 3444 cm<sup>-1</sup> and 3441 cm<sup>-1</sup> indicate -OH groups, enhancing hydrophilicity, useful for charge transfer and heavy metal ion adsorption. Peaks at 3043 cm<sup>-1</sup> and 2923 cm<sup>-1</sup> suggest preserved aromatic structures, while C=C double bonds (1588 cm<sup>-1</sup>, 1576 cm<sup>-1</sup>) contribute to conductivity. Peaks from 1143 cm<sup>-1</sup> to 1033 cm<sup>-1</sup> indicate C-O bonds, suggesting hydroxylation or oxidation products, crucial for pseudocapacitance mechanisms. GT/Ni500 has more functional groups but lower thermal stability than GT/Ni700. XPS spectra (Figure 4c) show characteristic peaks at 284.80 eV for both GT/Ni500 and GT/Ni700, indicating sp<sup>2</sup> hybridized carbon. Peaks at 290.08 eV (GT/Ni700) and 290.81 eV (GT/Ni500) confirm graphene formation. Raman spectra (Figure 4d) show D, G, and 2D bands at 1350, 1580, and 2715 cm<sup>-1</sup>. High D band intensity indicates significant defects, with D/G ratios of 2.64 (GT/Ni500) and 3.11 (GT/Ni700), suggesting more defects in GT/Ni700. The G band intensity indicates well-structured graphite, and the 2D band confirms single or few-layer graphene, consistent with TEM analysis.



Figure 4 Characterization of GT/Ni500 and GT/Ni700 materials using various analytical techniques:a) XRD patterns showing the crystalline structure of GT/Ni500 and GT/Ni700; b) FTIR spectra illustrating the functional groups present in PT, GT/Ni500 and GT/Ni700; c) XPS spectra depicting the elemental composition and chemical states of GT/Ni500 and GT/Ni700; d) Raman spectra revealing the vibrational modes and structural characteristics of GT/Ni500 and GT/Ni700.

### **Electrochemical performance of GT/Ni**

The GT/Ni obtained from catalytic pyrolysis

encapsulates NiF within multilayer graphene oxide, eliminating the need for additional electrode fabrication. Mass-normalized CV curves (Figure 5a) show that both GT/Ni500 and GT/Ni700 exhibit double-layer capacitance with rectangular shapes, though GT/Ni700's CV slightly deforms at higher scan rates, indicating good rate performance. A weak redox peak in GT/Ni500 and a stronger one in GT/Ni700 suggest pseudocapacitance from oxygen-containing functional groups. GCD curves (Figures 5b, 5c) reveal polarization, deviating from ideal double-layer behavior, confirming pseudocapacitance. GT/Ni700 demonstrates superior electrochemical performance, with a specific capacitance of 3342.45 mF/g at 0.5 A/g compared to 345 mF/g for GT/Ni500, retaining 29.22% at 2 A/g versus 10.14% for GT/Ni700. Nyquist plots (Figure 5e) show both materials have low Rs and Rct values under 0.35  $\Omega$  and 1.00  $\Omega$ , respectively, with GT/Ni700 displaying superior conductivity and a smaller Rct  $(0.25 \Omega)$  and Rs  $(0.13 \Omega)$ . Bode plot analysis confirms that GT/Ni700 has a faster charge-discharge rate, closer to an ideal capacitor behavior.



Figure 5 Electrochemical performance of GT/Ni500 and GT/Ni700 in three-electrode system. a) CV curve of GT/Ni500; b) CV curve of GT/Ni700; c) GCD curve of GT/Ni500; d) GCD curve of GT/Ni700; e) Nyquist plots; f) Bode plots.

### **GT/Ni adsorption properties**

Figure 6 shows the adsorption capacities of GT/Ni500 and GT/Ni700 for  $Pb^{2+}$  and  $Cu^{2+}$ , reaching equilibrium

120 minutes. GT/Ni500 exhibited superior at performance, with adsorption capacities of 47.94 mg/g for Pb<sup>2+</sup> and 43.13 mg/g for Cu<sup>2+</sup>, attributed to its higher carbon content at 500 °C. Both materials followed pseudo-second-order kinetics, suggesting combined physical and chemical adsorption. Adsorption isotherm analysis showed a better fit to the Langmuir model, indicating monolayer adsorption. FTIR analysis revealed interactions between functional groups (e.g., C-O, C-N) and heavy metals, forming new bonds (e.g., Pb-O, Cu-O), confirming successful adsorption. GT/Ni700 exhibited stronger magnetic properties, with higher saturation magnetization and remanence, enhancing its efficiency and stability in adsorption and recovery. Magnetic hysteresis analysis demonstrated that GT/Ni700 maintained magnetism effectively, facilitating better adsorption recovery. Ultrasonic desorption-regeneration experiments showed that GT/Ni had over 75% recovery rates across three cycles, highlighting good regeneration performance for heavy metal removal.



Figure 6 Heavy metal adsorption performance of GT/Ni500 and GT/Ni700. a) Adsorption kinetics; b) Adsorption isotherms; c) Hysteresis curves; d) Regeneration adsorption

### Analysis of pyrolysis mechanism

The catalytic pyrolysis of PT on NiF to produce multilayer graphene oxide involves three stages (Figure 7). In the first stage, PT undergoes catalytic cracking, with reactions like deoxygenation, cracking, and reforming reducing oxygen content and breaking down large molecules into smaller compounds. Deoxygenation reactions, such as dehydration and decarboxylation, effectively remove oxygen, forming CO<sub>2</sub>, CO, and H<sub>2</sub>O. During the second stage, pyrolysis gases, including H<sub>2</sub> and CH<sub>4</sub>, act as deposition gases, facilitating graphene synthesis while potentially offsetting energy costs. Unlike traditional CVD

methods, high-temperature PT pyrolysis directly generates these gases, improving safety and efficiency. In the third stage, at 700 °C, carbon atoms deposited on NiF rearrange from sp<sup>3</sup> to sp<sup>2</sup> hybridization, forming graphene structures with fewer layers. This transformation enhances the electrical conductivity of GT/Ni700 compared to GT/Ni500, resulting in a material with improved performance.



Figure 7 Mechanism of multilayer graphene formation via pyrolysis.

### Analysis of environmental benefits

GT/Ni700 exhibits a specific capacitance of 3.34 F/g at 0.5 A/g, while the Langmuir fitting results indicate that GT/Ni500 has adsorption capacities of 59.86 mg/g for Pb<sup>2+</sup> and 56.84 mg/g for Cu<sup>2+</sup>. Both materials demonstrate effective performance as electrode sheets and adsorbents. A lifecycle assessment (LCA) comparing this study to Pandey et al. (2019), who produced multilayer graphene from waste plastic, reveals that our method has a smaller environmental footprint. Input and output data (S. Table 2) from Ecoinvent database (v3.8) show that, compared to Pandey's method, the overall lifecycle impact on human health, ecosystems, and resources is reduced by over 51% (Figure 8). Our pathway outperforms in most of the 18 environmental impact categories, with significant reductions in CO2 equivalents for electrode and adsorbent preparation. Specifically, GT/Ni700 and GT/Ni500 have lower CO2 equivalents (17.64 kg/CO2eq, 16.06 kg/CO2eq, and 14.03 kg/CO2eq, 12.81 kg/CO2eq, respectively) compared to Pandey's method, reflecting lower environmental toxicity and climate impact. Thus, this study presents a more sustainable approach to producing high-value multilayer graphene materials, enhancing the comprehensive utilization of PT.



Figure 8 Life cycle assessment of aifferent graphene production methods. a, b) life-cycle energy demand and climate change impacts; c) and a comparison of the corresponding environmental costs of producing 1 cm2 of GT/Ni.

### CONCLUSION

This study demonstrates the feasibility and environmental advantages of converting PT into high-quality multilayer graphene oxide using NiF as a catalyst. The catalytic pyrolysis at 500 °C and 700 °C effectively decomposes PT and facilitates the structured rearrangement of carbon atoms into graphene layers. Comprehensive characterization confirms the formation of multilayer graphene oxide, exhibiting remarkable electrochemical performance and significant heavy metal adsorption capacities. GT/Ni700 exhibits a high specific capacitance of up to 3.34 F/g, while GT/Ni500 shows exceptional adsorption capacities of 59.86 mg/g for Pb2+ and 56.84 mg/g for Cu2+, demonstrating the dual utility of the synthesized materials in electrochemical applications and environmental remediation. LCA results highlight a substantial reduction in the carbon footprint, with CO<sub>2</sub> equivalents for GT/Ni500 and GT/Ni700 significantly lower than those of traditional methods. This innovative approach not only enhances the value of PT but also reduces greenhouse gas emissions and reliance on non-renewable resources. By providing a sustainable pathway for PT utilization, this study contributes to addressing pressing environmental issues and promoting the development of advanced materials with broad industrial applications.

# INSIGHTS INTO BIOAEROSOL CONTAMINATION IN THE PROCESS OF MINERZLIZED REFUSE MINING: MICROBIAL AEROSOLIZATION BEHAVIOR AND POTENTIAL PATHOGENICITY

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### ABSTRACT

The landfill mining process is a main source of anthropogenic bioaerosol release, posing potential risks to the health of occupationally exposed personnel and nearby residents. In this study, microbial aerosolization behavior and potential pathogenicity during the landfill mining process were systematically investigated. The highest concentration of bacterial aerosols was measured in the refuse mining area, with a value of  $5968 \pm 1608$  CFU/m<sup>3</sup>, while the highest concentration of fungal aerosols was  $1196 \pm 370$  CFU/m<sup>3</sup> in the refuse screening area. The bacterial and fungal aerosols were distributed primarily in the particle size ranges of  $4.7 \sim 7.0 \ \mu m$  and  $> 7.0 \ \mu m$ , respectively. The pathogenic microbes Arthrobacter, Bacillus, Arthrobotrys and Aspergillus had high bioaerosol aerosolization capacities. There are more than 100 types of pathogenic bacteria in bioaerosols. The microorganisms Lysobacter, Luteimonas and Mycolicibacterium, which carry virulence factor genes (VFGs) (pilG, Rv0440, pilT, etc.), can spread VFGs, aggravate bioaerosol pollution, and threaten the health of workers and nearby residents. This research will help further the understanding of bioaerosol contamination behaviors and potential pathogenicity risks from landfill mining activities.

**KEYWORDS:** landfill mining; bioaerosols; aerosolization behavior; virulence factor genes; pathogenicity

### **1. INTRODUCTION**

Landfills are effective technologies for the safe disposal of municipal solid waste (MSW) but occupy a large amount of land and cause a series of environmental pollution problems such as leachate leakage, odor nuisance and greenhouse gas emissions (Qian et al., 2024; Wijekoon et al., 2022). It has been estimated that over the past few decades the amount of accumulated domestic garbage has reached as much as 8 billion tons occupying approximately 550 million square meters of land, and landfill facilities have become a new risk point for the ecological environment (National Bureau of Statistics in China). Mineralized refuse mining, which can support material recycling and land resource regeneration and address the long-term environmental pollution and potential safety hazards of landfills, is one of the most important ecological management methods for landfills (Einhäupl et al., 2021).

The degradation of refuse provides an ideal environment for the growth of various microorganisms. Pathogenic bacteria that can cause cancer, immune system diseases, infectious diseases, etc., are widely distributed in landfills (Wang et al., 2021). During landfill activities (such as dumping, digging, and rolling) microorganisms attached to the surface of refuse particulate matter (PM) can enter the atmosphere and spread around the landfill site forming bioaerosols after aerosolization (He et al., 2019). These bioaerosols contain water-soluble also ions, heavy metals, microorganisms and other pathogenic harmful substances (Shen and Yao, 2023; Zhang et al., 2023). Therefore, landfills are considered major anthropogenic sources of bioaerosols which can seriously harm the health of occupational personnel and nearby residents (Liu et al., 2023; Nair et al., 2021).

Research has been carried out on the pollution characteristics and potential risks of bioaerosols in sanitary landfills. The concentrations of bioaerosols in landfill areas fluctuates from hundreds of CFU/m3 to tens of thousands of CFU/m<sup>3</sup>, and are closely related to the degree of operation disturbance and meteorological conditions in the landfill area (Breza-Boruta, 2016; Liu et al., 2023). Moreover, there are many types of microorganisms in landfill bioaerosols that can induce allergic pneumonia and other respiratory diseases, such as the bacterial genera Streptococcus, Clostridium, Staphylococcus and Bacillus and the fungal genera Aspergillus and Streptomyces (Cyprowski et al., 2019). Unlike MSW landfills, the main goal of landfill mining is the processing of mineralized refuse and the composition and physicochemical properties of mineralized refuse are significantly different from those of fresh waste (Faitli et al., 2019); therefore, bioaerosol behaviors in the landfill mining process, including bioaerosol concentration, particle size distribution, and microbial community structure, are different from those in the MSW landfill process.

Most bioaerosols have particle sizes ranging from microns to submicrons. They can be suspended in the air for lengthy periods and spread far from their source. Li et al. (2021a) reported that the particle size of airborne bacterial aerosols in landfills was mainly 1.1~4.7 µm, while most fungal aerosols had particle

sizes > 4.7  $\mu$ m. Morgado-Gamero et al. (2021) reported that the concentration of bacterial aerosols with fine particles with an aerodynamic diameter of 1.0~5.0  $\mu$ m was highest in active landfill units. The aerodynamic size of particles determines their penetration and deposition depth in the human respiratory system, which in turn determines their possible health effects. The smaller the particle size, the deeper it can penetrate the respiratory system, especially within the particle size range that may pose a health threat to the alveoli and distal bronchi (Madhwal et al., 2020). However, there are few reports about the distribution of bioaerosol particles and their harmful effects on the respiratory system during the landfill mining process.

The harmful effects of bioaerosols on human health are determined mainly by the toxic effects of aerosols carrying pathogenic microorganisms into the human body. The potential pathogenic risk of bioaerosols depends mainly on the biological activity, biomass and virulence of important pathogenic bacteria (Kim et al., 2018). Concerns are growing about bioaerosol pollution risk assessment involving human bacterial pathogens (HBPs) and virulence factor genes (VFGs) as important assessment targets (Kang et al., 2023; Yang et al., 2020). MSW landfills have been implicated as major sources and transmission vectors for VFGs and HBPs (Wan et al., 2021), and the coexistence of VFGs in HBPs increases the risk of bioaerosol pollution in the landfill mining process. Therefore, the risk of bioaerosol contamination in landfill mining activities, including the occurrence characteristics and coexistence characteristics of HBPs and VFGs, needs to be taken seriously. However, limited research has been conducted on this topic.

In this study, the microbial aerosolization behavior and potential pathogenicity during the landfill mining process were systematically investigated. The aims of this study were (1) to evaluate the contamination characteristics of bacterial and fungal aerosols (including the emission concentration, and particle size distribution) during the landfill mining process; (2) to identify the main potential pathogens in the bacterial and fungal aerosols and their diversity and abundances; and (3) to study the occurrence characteristics and coexistence characteristics of HBPs and VFGs in mineralized refuse and bioaerosols. This research will help researchers to comprehensively understand bioaerosol contamination behaviors and potential pathogenicity risks from landfill mining activities.

### 2. MATERIALS AND METHODS

### 2.1 Sampling site

The subject MSW landfill site is located at  $109^{\circ}10'33''E$  and  $27^{\circ}44'00''N$  in Guizhou Province, China. The landfill serves approximately 105,900 people in the surrounding towns. The designed service life of the landfill is 11 years, the landfill area is approximately 18748 m<sup>2</sup>, and the fill volume is

approximately 310,000 m<sup>3</sup>. The main landfill mining projects include aerobic accelerated stabilization, stabilized refuse excavation, refuse screening and material disposal, as well as deodorization and leachate treatment. The landfill age of the excavated mineralized refuse was 10~11 years during the sampling period.

To determine the pollution characteristics of bioaerosols during mineralized refuse mining, four sampling points including the excavation area, the screening area, the upwind direction of the plant boundary and the downwind direction of the plant boundary were selected (Fig. 1), as described by Kang et al. (2023) and Li et al. (2021a). At the excavation area, an excavator was continuously operated for 4 hours with an excavated refuse quantity of approximately 8~10 t/h. In the screening area, the screening machine was continuously operated for 4 hours with a sieve weight of approximately 5~8 t/h. The sampling points in the upwind direction and downwind direction of the plant boundary were both 150 m away from the refuse excavation point.



Fig. 1 The sampling sites of bioaerosols during landfill mining

# 2.2 Collection of bioaerosols and aerosol particles on the filter membrane

Culturable bacterial and fungal aerosols were collected with an Andersen six-stage air microbial sampler (FA-1, Zhengzhou Zhaowei Instrument Equipment Co., Ltd.) during the landfill mining period. The capture particle size was divided into six levels (L1 to L6) with aerodynamic diameters > 7.0  $\mu$ m (L1), 4.7~7.0  $\mu$ m (L2), 3.3~4.7  $\mu$ m (L3), 2.1~3.3  $\mu$ m (L4), 1.1~2.1  $\mu$ m (L5) and 0.65~1.1  $\mu$ m (L6), corresponding to different parts of the human respiratory system.

For sampling of culturable bacterial and fungal aerosols, nutrient agar plates (10 g of tryptone, 5 g of yeast extract, 10 g of sodium chloride, 15 g of agar powder, and 1000 mL of distilled water) and Cha's agar plates (3 g of sodium nitrate, 1 g of dipotassium hydrogen phosphate, 0.5 g of magnesium sulfate, 0.5 g of potassium chloride, 0.01 g of ferrous sulfate, 30 g of sucrose, 20 g of AGAR powder, and 1000 mL of distilled water) were placed on an Andersen impactor. The impactor was operated at a flow rate of 28.3 L/min, with a sampling time of 5 minutes for bacteria and 15 minutes for fungi. After sampling, the corresponding culture conditions for bacteria and fungi were 37 °C for 24~48 h and 28 °C for 72~120 h, respectively. Parallel samples were collected at each point.

In addition, aerosol particles of different sizes released at mining points were collected with a polycarbonate filter membrane (pore diameter  $0.22 \mu m$ , 80 mm in diameter) using an Andersen six-stage air microbial sampler (Zhang et al., 2024). The air particle samples were collected at a flow rate of 28.3 L/min and continuously sampled for 4 hours. Four filter membranes were collected for each sampling level (L1L6) to obtain sufficient air particles. The collected samples were stored at -80 °C for further microbial (including culturable and unculturable microbes) analysis. The mineralized refuse and leachate at the excavation site were also collected.

Before sampling, each stage sampler was carefully and thoroughly wiped with 75% ethanol and allowed to dry naturally. During sample collection, the operators wore gloves and masks to reduce human interference. At all sampling points the sampler was placed on a tripod at an average human respiratory height of 1.50 m above ground level. Meteorological conditions such as temperature, relative humidity (RH), wind speed and ambient air quality monitoring indices (CO, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub>), were simultaneously obtained at each sampling point during the sampling period.

### 2.3 Microbiological analysis

#### **2.3.1** Concentration of culturable bioaerosols:

After cultivation, the colonies of culturable bacteria and fungi on the six Petri dishes were counted, and the counting results were corrected according to Feller's statistical correction table. According to the air sampling volume the number of culturable bioaerosols at each of the six levels was calculated in colony forming units (CFU/m<sup>3</sup>) per cubic meter of air using the following equation: (Liu et al., 2021):

$$C = \frac{N \times 1000}{Q \times T} \tag{1}$$

where C represents the concentration of bioaerosol (CFU/m<sup>3</sup>), N represents the colony forming unit (CFU), Q represents the sampling flow rate (L/min), and T represents the sampling time (min).

# 2.3.2 Microbial diversity and community structure of bioaerosols:

The samples of culturable bioaerosols, aerosol particles on the filter membrane after ultrasonic treatment (Geng et al., 2024), mineralized refuse and leachate were subjected to DNA extraction using a soil microbial DNA extraction kit (Mobio/Qiagen, USA) according to the manufacturer's instructions. The concentration and purity of the DNA were measured

with a Nanodrop 2000 (Thermo, USA). The high-quality DNA samples were sent to Sangon Biotech (Shanghai) Co., Ltd., for high-throughput sequencing. The bacteria and fungi in the samples were sequenced on an Illumina MiSeq high-throughput sequencing platform (Wang et al., 2023). The bacterial 16S rDNA from V3~V4 was amplified with the primers 341F (CCTACGGGNGGCWGCAG) 805R and (GACTACHVGGGTATCTAATCC). The fungal regions amplified were ITS1~ITS2, with the primers ITS1F (CTTGGTCATTTAGAGGAAGTAA) and ITS2 (GCTGCGTTCTTCATCGATGC). The microbial diversity and community structure of the bioaerosols were analyzed with mothur software.

### 2.3.3 Metagenomic sequencing:

Metagenomic sequencing was conducted for the samples enriched with air particles on polycarbonate filter membranes (aerosol particle samples >7.0 µm; only the first level met the library construction requirements), and mineralized refuse and leachate samples on the Illumina NovaSeq 6000 platform. Fastp (v.0.36) was used to evaluate the quality of the sequencing data. First, Megahit (v.1.2.9) was used for multisample mixed splicing to obtain the initial spliced overlapping group sequence. Then, Bowite2 (v.2.1.0) was used to map the clean readings back to the concatenated results, the unmapped readings were extracted, and SPAdes (version 3.13) was used for concatenation to obtain low-abundance overlapping groups. MetaWRAP (v.1.3.2) was used to perform a series of boxing operations. After packing, gene prediction, gene set construction, gene set abundance, gene set functional annotation, and abundance analysis were performed. The double enzyme algorithm and the method of constructing a bias model were used to accurately quantify the gene abundance in each sample. DIAMOND (v.0.8.20) was used to compare the gene set with databases (Bağci et al., 2021). All of the filtered metagenomic sequencing data were mapped with the virulence factor database to categorize the types of virulence factor genes (VFGs).

### 2.4 Statistical analysis

Bar charts showing the abundances of microbes, VFGs and HBPs were generated using OriginLab 2021 (OriginLab Corporation, USA). A network graph was drawn to visualize the interactions among the VFGs and microbes.

### **3. RESULTS AND DISCUSSION**

3.1 Pollution characteristics of culturable microorganisms in bioaerosols during landfill mining

### <u>3.1.1 Concentration of culturable bacteria and</u> <u>fungi aerosols and influencing factors:</u>

The total concentrations of culturable bacterial and fungal aerosols in different areas during landfill mining were compared, as shown in Fig. 2. The highest concentration of bacterial aerosols in the refuse mining area was 5968  $\pm$  1608 CFU/m<sup>3</sup>, while the highest concentration of fungal aerosols was  $1196 \pm 370$ CFU/m<sup>3</sup> in the refuse screening area, both significantly greater than those in the plant boundary area. The concentrations of bacterial and fungal aerosols were  $3512 \pm 634$  CFU/m<sup>3</sup> and  $720 \pm 106$  CFU/m<sup>3</sup> downwind of the landfill boundary, respectively, significantly greater than those at the sampling point upwind of the landfill boundary. Overall, the bioaerosol concentration decreased in the order of upwind of the landfill boundary < downwind of the plant boundary < mechanical operation area. The mining and screening operations of mineralized refuse results in the direct release of microorganisms to form bioaerosols (Frączek et al., 2017) and meteorological conditions such as

wind cause bioaerosols to spread outside of the plant boundary (Ali et al., 2022).

Generally, the abundance of airborne bacteria is greater than that of fungi in landfills (Akpeimeh et al., 2019), and the bioaerosol abundance is significantly greater in active areas of landfills than in other areas (enclosed areas, boundary areas and leachate treatment areas), consistent with our experimental results (Frączek et al., 2017). However, owing to the different physical and chemical properties of waste, landfill construction conditions and meteorological conditions, the bioaerosol concentrations at different landfills greatly differ.



Fig. 2 The total concentrations of bacterial and fungal aerosols in different sampling areas during the landfill mining process

The results of the correlation analysis between bioaerosol concentration and environmental factors are shown in **Fig. 3**. The concentration of bacterial aerosols was significantly positively correlated with temperature, RH, and PM and negatively correlated with CO and O<sub>3</sub>. The fungal aerosol concentration (L1~L4 level) was strongly positively correlated with RH and PM but strongly negatively correlated with wind speed and O<sub>3</sub>. During the refuse mining process bacteria and fungi are attached to the fine particles of refuse suspended in the air, resulting in a strong positive correlation between the bioaerosol concentration and the PM concentration (Yin et al., 2021). Appropriate temperature and humidity are conducive to the growth and reproduction of bacterial and fungal aerosols (Han et al., 2020; Yin et al., 2021), while high concentrations of CO and O<sub>3</sub> are toxic to bacterial activity in the air (Abdel et al., 2012). Strong winds favor the diffusion of bioaerosols, resulting in a high concentration of bioaerosols downwind of the plant boundary (Li et al., 2021b).



Fig. 3 Correlation between aerosol concentrations of culturable bacteria (a) and fungi (b) and environmental factors

### 3.1.2 Size distribution of culturable bioaerosols

### and risk assessment:

The aerodynamic diameter of biological aerosols is key to the potential risks of their diffusion, inhalation, and disposal in the trachea, bronchus, or alveolar region (Nair et al., 2021). The number and percentage of bioaerosols in different particle size segments according to the six particle size ranges are presented in Fig. 4.

The size distribution revealed a large number of bacterial aerosols with aerodynamic diameters >4.7  $\mu$ m in the refuse mining area and screening area, accounting for 53% and 61%, respectively, of total bacterial aerosols. This indicates that bacterial aerosols > 4.7  $\mu$ m are more easily transported with dust during landfill mining and screening activities and that these particles can accumulate in the nose and throat of the human body. The percentage of fine bacterial aerosols

(ranging from 0.65~1.1 µm) in the mining area was also high, accounting for 17% of the total bacterial aerosol concentration. These particles may accumulate in the upper part of the respiratory system and in the alveoli, causing allergic alveolitis after inhalation via contact (Cyprowski et al., 2019). Li et al. (2021a) reported that bacterial aerosols were mainly distributed with an aerodynamic diameter of 1.1~4.7 µm in a sanitary landfill, possibly because the mineralized refuse properties and microbial composition were quite different from those of fresh refuse (Wang et al., 2021). Notably, fine particle-size bacterial aerosols (0.65~2.1 µm) also occupied a large proportion of the plant boundary area. This was due to the poor sedimentation performance of fine particles which tend to be suspended in the atmosphere and spread to distant regions with wind (Yang et al., 2020).



Fig. 4 Particle size distribution of the culturable microorganisms at each sampling point

Similar to the distribution characteristics of the bacterial aerosols, the fungal aerosol particles in the mechanical operation area were mainly distributed with an aerodynamic diameter >4.7  $\mu$ m, accounting for approximately 60% of the total fungal aerosol concentration. In contrast to bacterial aerosols, fungal aerosols do not have a high percentage of fine particles (0.65~1.1  $\mu$ m) downwind of the plant boundary, partly related to the large particle size of the fungi themselves, as microorganisms with large particle sizes are more likely to settle under the action of gravity (Li et al., 2021b).

Overall, the bacterial and fungal aerosols were mainly distributed in the particle size ranges of  $4.7 \sim 7.0$  $\mu$ m and > 7.0  $\mu$ m, respectively, and were more likely to have entered the oral cavity, nasal cavity and pharynx of occupationally exposed persons. In the excavation area and downwind direction of the plant boundary, the concentration of cultivable bacteria in fine particles  $(0.65\sim1.1 \ \mu\text{m})$  was also greater. These aerosol particles may accumulate in the upper part of the respiratory system and alveoli (Morgado-Gamero et al., 2021), posing a health risk to both occupationally exposed persons and surrounding residents.

# 3.2 Characteristics of the microbial community structure in bioaerosols

### <u>3.2.1 Composition of culturable microbial</u> <u>communities in bioaerosols:</u>

The compositions of the culturable microbial communities in the bioaerosol, mineralized refuse and leachate samples at the genus level are shown in **Fig. 5**.

In the bacterial aerosol samples, *Arthrobacter* and *Bacillus* were the most common genera and *Pseudomonas* was also highly abundant in the L5 and L6 samples (Fig. 5(a)). However, unclassified and other genera accounted for very high proportions.

Arthrobacter is widely distributed in the natural environment and has the ability to survive long term conditions caused by under stress starvation, temperature changes, ionizing radiation, and toxic compounds (Guo et al., 2019). Bacillus species also exhibit strong resistance to harmful external factors and exist in soil, water, air and other places in nature (Qian et al., 2023). The superior adaptability of these genera enables them to survive during the landfill mining process and become the dominant genera in bioaerosol samples. In contrast, Nitrosomonas, Luteimonas, and Galbibacter were culturable bacteria detected in mineralized refuse and leachate samples but not in bioaerosol samples, indicating that they were not well adapted to sudden changes in their environment and could not survive in atmospheric aerosols. **(a)** 

> 100 Relative Abundance (%) 20 L1 L2 L3 L4 L5L6 MR RL Spor Plan Lute Pseudomona Streptomyces Galbibacter Other Acinetobacter Arthrobacter Nitrosomonas (c) 10 Relative Abundance (%) 20 L1 L2 L3 L4 L5 L6 MR RL Bacillus Chryseomicrobium Planomicrobium
>  Galbibacter Lysobacter Sphingomonas
>  Rhodanolacter Allererythrobacter
>  Nitrosomonas Unclassified Others Muricauda

There were significant differences in the dominant fungi at different levels in the bioaerosol samples (Fig. 5(b)). Arthrobotrys and Alternaria were the dominant fungal genera in the L1 and L2 samples, Penicillium was overwhelmingly dominant in the L4 sample and Aspergillus was the dominant genus in the L3, L5 and L6 samples. Rhizopus, Orbilia and Mucor were the common genera in the mineralized refuse and leachate samples but were not detected in the bioaerosol samples, indicating that they were not adapted to changes in the living environment. Similarly, some genera such as Pseudallescheria, Debaryomyces, Alternaria and Penicillium were detected in the bioaerosol samples but not detected in the mineralized refuse and leachate, suggesting that they might be derived mainly from the atmospheric environment. (b)



**Fig. 5** Composition of culturable bacterial (a) and fungal (b) communities in bioaerosols and bacterial (c) and fungal (d) communities in aerosol particles on the filter membrane at genus level

# 3.2.2 Composition of microbial communities in aerosol particles on the filter membrane:

The microbial community structures of bacteria and fungi at the genus level in the six levels of aerosol particles in the landfill mining area are shown in Fig. 5(c) and (d).

At the genus level, Galbibacter, Lysobacter, Muricauda, and Rhodanobacter were the top four bacterial genera in the mineralized refuse sample. In the >7 µm bacterial aerosols, Galbibacter, Arthrobacter, Planomicrobium and Chryseomicrobium were the most common genera and Sphingomonas, with a high abundance, was also detected in the L5 sample. The potentially pathogenic genera Arthrobacter and Sphingomonas were detected. Specifically, Arthrobacter exists widely in soil and other environments and members of this genus may cause human bacteremia and infective endocarditis (Li et al., 2021c). As an organic degrading strain, Sphingomonas is widely present in both natural and artificial water environments which may lead to a high proportion of these bacterial species in the surrounding air, causing a series of infections, including pneumonia, meningitis, catheter-related bloodstream infections, and wound infections (Johnson et al., 2018). In addition, relatively low proportions of Bacillus and Microbacterium may also be harmful to humans. For example, Bacillus cereus can cause food poisoning in humans and animals (Jovanovic et al., 2021), while Microbacterium can cause acute lymphocytic leukemia in children (Amano et al., 2019).

Among fungi, *Rhizopus* dominated in the mineralized refuse, possibly originating from plant residues, decaying organic matter, animal manure, and soil. The dominant genera in the bioaerosol samples included *Arthrobotrys*, *Pseudallescheria*, *Aspergillus* 

and Debaryomyces. Pseudallescheria is widely present in soil, sewage, and decaying organic matter (Luplertlop, 2018). Aspergillus is one of the main microorganisms causing mold rot of various substances (Khan et al., 2024), and studies have found that Aspergillus is dominant in bioaerosol samples (Cyprowski et al., 2019; Morgado-Gamero et al., 2021). The relative abundance of these two microorganisms may be related to the decay process and fermentation stage of solid waste in landfills. Most identified fungi have multiple adverse health effects and can cause allergies, asthma, and bronchial and pulmonary infections. As one of the most common genera, Aspergillus can induce allergic and asthmatic lung diseases resulting in high mortality rates, with over 200000 life-threatening Aspergillus infections occurring worldwide each year (Sabino, 2022). These fungi exist in the air around landfills and their small size allows them to spread throughout the entire respiratory system, posing a threat to the health of residents or other organisms in the surrounding area.

3.2.3 Differences in microbial communities between culturable bioaerosol and aerosol particles on the filter membrane:

Differences in the microbial communities between the culturable bioaerosol and aerosol particles on the filter membrane in the excavation area were compared, as shown in **Fig. 6**. As a pathogenic genus, the proportions of culturable *Arthrobacter* in the L1, L2, L3, L4, and L6 samples were greater than those in the aerosol particles on the filter membrane, indicating that *Arthrobacter* is more likely to accumulate and multiply in nutrient-rich environments (Sutthiwong et al., 2023). Cultivable *Bacillus* had an absolute advantage in the L5 sample, indicating that *Bacillus* attached to particles with an aerodynamic diameter of  $1.1\sim2.1 \ \mu m$  easily survived and may be likely to enter human terminal bronchi during landfill mining. In addition, some culturable bacteria such as *Planomicrobium* and *Chryseomicrobium*, which tend to grow in high-salt environments, account for large proportions of the aerosol particles on the filter membrane, but they cannot survive in the atmospheric environment and may pose little threat to human health.

In the L1 and L2 samples *Alternaria* occupied only a low proportion of the aerosol particles but occupied the largest proportion of the culturable fungal aerosols. A similar phenomenon was observed for *Penicillium* in the L4 sample and *Aspergillus* in the L3, L5 and L6 samples. These results indicate that these fungi were more likely to survive in these particle size ranges and easily adapted to changes in their environment. Culturable *Arthrobotrys* was the dominant genus in the aerosol particles on the filter membrane but was not detected in the culturable aerosols, indicating that they had a low ability to survive in the atmospheric environment and were not able to grow easily and reproduce.



Fig. 6 Differences in microbial communities between culturable microorganisms and aerosol particles on the filter membrane (a) bacteria (b) fungi

Under the pressures of landfill mining (such as changes in ultraviolet radiation, temperature and salinity) some microorganisms have a strong ability to resist adverse external environments and exist in the form of active cells, while some are greatly affected by adverse environments and are present only in the form of cell debris, and some are composed primarily of cellular metabolites or gene fragments (Wu et al., 2024; Shen and Yao, 2023). In the process of landfill mining, culturable pathogenic bacteria of *Arthrobacter* and *Bacillus* and fungi of *Alternaria, Aspergillus* and

*Penicillium* are more likely to survive in the surrounding environment of the landfill, and they may pose a severe health threat to landfill workers and residents.

### 3.3 Potential human pathogens in bioaerosols

A total of 109, 114 and 72 kinds of HBPs were detected in the bioaerosol particles on the filter membrane (>7  $\mu$ m), mineralized refuse and leachate samples, respectively. HBPs identified in the bioaerosol particles were highly similar to those in the mineralized refuse sample. A total of 108 kinds of HBPs were the same as those in the mineralized refuse, indicating that mineralized refuse was the direct source of pathogenic bacteria in bioaerosols. Compared with bacterial pathogens, fewer fungal pathogens were detected in the experimental samples. Five, four and two kinds of human fungal pathogens were detected in the bioaerosol particles on the filter membrane (>7  $\mu$ m), mineralized refuse and leachate samples, respectively. Emerging and re-emerging human pathogens such as *Enterococcus faecalis, Pseudomonas aeruginosa, Staphylococcus aureus, Serratia marcescens*, and *Streptococcus pneumoniae* have been identified in bioaerosol particles, posing a potential threat to human health and public safety.

The relative abundance of pathogenic microbes in the different samples is shown in **Fig. 7**. The proportions of HBPs in the bioaerosol particles on the filter membrane (>7 µm), mineralized refuse and leachate samples were very low, 0.41%, 0.56% and 0.45%, respectively. Pseudomonas aeruginosa, Stenotrophomonas maltophilia, Escherichia coli, Klebsiella oxytoca and Vibrio cholerae were the dominant pathogenic bacteria in the bioaerosol particles on the filter membrane. These pathogenic bacteria can invade the human respiratory tract or intestinal tract and are highly pathogenic to humans and animals because they cause human pneumonia, gastrointestinal tract disorders and other diseases (Nadalian et al., 2020; Neog et al., 2021). Some low-abundance pathogenic bacteria can also cause human diseases. For example, Bacillus cereus can cause food poisoning, serious infection and bacteremia in humans (Saigal et al., 2016), and Nocardia farcinica can cause pneumonia in immunocompromised patients (Beucler et al., 2022).



**Fig. 7** Species and relative abundance of pathogenic bacteria in the bioaerosol particles on the filter membrane (> 7 um), mineralized refuse and leachate samples (a) bacteria (b) fungi

The proportion of fungal pathogens was relatively high and the proportions of fungal pathogens in the bioaerosol particles on the filter membrane (>7  $\mu$ m), mineralized refuse and leachate samples were 4.44%, 22.14%, and 4.77%, respectively. Five fungal pathogens including *Beauveria bassiana*, *Chaetomium* globosum, *Fusarium proliferatum*, *Madurella mycetomatis*, and *Rhizopus microsporus*, were detected in the bioaerosol particles on the filter membrane (>7 μm). These fungi may spread by spore aspiration or wounding and are prone to attack immunocompromised patients, which can cause damage to the sinuses, lungs and brain (Sun et al., 2018).

The airborne transmission of pathogens occurs because pathogens can induce disease through the inhalation route. The potential pathogenic risk of bioaerosols in landfill mining depends mainly on the biological activity, biomass and virulence of important pathogenic microbes (Wu et al., 2024). Although the relative abundance of pathogens was relatively low their potential health risks cannot be ignored.

### 3.4 Occurrence characteristics of VFGs loaded with

**bioaerosols** 

Tracking the bacterial hosts of VFGs is vital for understanding the potential for pathogenicity in microbial ecosystems, as the hosts are critical for determining their risk to human health (Kang et al., 2023). Studies have provided evidence for the occurrence of HBPs in landfills, and the increased pathogenicity of HBPs carrying VFGs is critical for assessing the virulence risk of bioaerosols (Hui et al., 2023). Information about the occurrence characteristics of VFGs and their relationships with the HBPs during the landfill mining process is shown in **Fig. 8**.



**Fig. 8** Distribution characteristics of VFGs in the bioaerosol particles on the filter membrane (> 7 um) and mineralized refuse and their relationship with hosts. (a) Total relative abundance of VFGs (b) Relative abundance of VFGs (c) Changes in the abundance of VFGs in bioaerosol particles compared to mineralized refuse (d) The top ten VFGs in hosts

There were 243 and 241 VFGs detected in the bioaerosol particles on the filter membrane and

mineralized refuse, respectively. *pilT* was the most abundant VFG gene in the mineralized refuse sample, accounting for 13.3% of the total VFGs, followed by the pilG gene (11.4%). For the bioaerosol particles, the abundance of VFGs ranged from 1.20  $\times$  10<sup>-3</sup>~1.37  $\times$  $10^{-2}$ , with *Rv0440* having the highest abundance, 13.6%, followed by *pilG* and *pilT* (Fig. 8(a)). Virulence factors (VFs) are gene expression products (e.g., bacterial toxins, cell surface proteins and hydrolytic enzymes) of bacterial pathogens and can enhance pathogen establishment and pathogenicity (Liu et al., 2022). The VFs detected in all of the samples could be divided into ten categories, with stress proteins being the most common type (1.38%), followed by adherence, twitching motility and regulation. Similar results have shown that the VFs involved in adherence and stress survival are highly active in anaerobic digestion systems (Lin et al., 2022). In addition, many other VFs that may pose potential unknown risks to humans have not been identified (Fig. 8(b)). Notably, the abundance of most VFs in bioaerosol particles was lower than that in mineralized refuse (Fig. 8(c)), but the abundance of VFs involved in cellular metabolism and anaerobic respiration was greater than that in mineralized refuse. VFs play vital roles in pathogenesis by interfering with the normal metabolism of cells, inhibiting respiration and leading to damage and even death of host cells (Liu et al., 2022). These results show that the VFGs in bioaerosol samples exhibited high invasiveness and competitive advantages, which increased the pathogenicity of VFG hosts (Zhu et al., 2022).

The bubble plots of the top ten VFGs show that the dominant VFGs are related mainly to the assumed hosts of *Mycolicibacterium* (*Rv0440*, *glnA1*, *narG*, *narH*), *Lysobacter* (*pilT*, *pilB*, *xpsE*, *pilU*, *pilB*), *Luteimonas* (*pilT*, *pilB*, *katA*, *xpsE*, *pilG*), and some unclassified bacteria (Fig. 8(d)). The dangers of bacteria are usually closely related to VFGs. The presence of various and highly abundant VFGs in these hosts increases the ability of these microorganisms in bioaerosols to cause infections after being inhaled (Han et al., 2019; Kang et al., 2023). Therefore, microorganisms carrying VFGs in bioaerosols formed during landfill mining processes pose a high risk to human health.

Network analysis was used to explore the co-occurrence patterns of assumed hosts and VFGs, as shown in Fig. 9. In the mineralized refuse sample network there were 34 nodes in the top ten VFGs and host network correlation diagrams, and *pilT* and *pilG* were the dominant VFG types. Luteimonas was strongly associated with various VFGs and Lysobacter was also strongly associated with various VFGs. Among the bioaerosol particles, 33 nodes were among the top ten VFGs and hosted network correlation Lysobacter, diagrams. Luteimonas, and Mycolicibacterium were the top three hosts with strong associations with various VFGs. Among these, Lysobacter accounted for more than 1% of the bacteria, with a high potential for spreading VFGs and aggravating bioaerosol pollution (Zhu et al., 2022).



**Fig. 9** Correlation diagram of the top ten VFGs and hosts network (a) mineralized refuse (b) bioaerosol particles on the filter membrane (> 7 um)

*PilG* and *pilT* were present mainly in the HBP of *Pseudomonas aeruginosa PAO1*, and *Rv0440* was present mainly in the HBP of *Mycobacterium tuberculosis H37Rv*. These results suggest that pathogenicity and VFGs are enriched with the enrichment of HBPs in bioaerosols. The high prevalence and activity of these two pathogens also suggest a high chance for them to acquire the surrounding VFGs, thus aggravating their threats to human health and environmental safety (Kang et al., 2023).

Overall, more than 100 pathogenic bacteria were present in the bioaerosol formed during the landfill mining process and a variety of dominant pathogens could be cultured. Pseudomonas aeruginosa, Stenotrophomonas maltophilia, Escherichia coli, Klebsiella oxytoca and Vibrio cholerae were the dominant pathogenic bacteria in the samples. In addition, microorganisms carrying VFGs (pilG, Rv0440, pilT, etc.) in bioaerosol samples, such as Lysobacter, Luteimonas and Mycolicibacterium, can spread VFGs

and aggravate bioaerosol pollution, which further threatens the health of workers and nearby residents.

### 4. CONCLUSIONS

Landfill mining can release high concentrations of bioaerosols, and bioaerosols pose high health risks to occupationally exposed personnel during refuse excavation and screening activities. The environmental factors of temperature, RH, and PM strongly affect the concentration of bioaerosols formed during landfill Arthrobacter, mining activities. Bacillus and Pseudomonas were the most common bacterial genera Arthrobotrys, Alternaria, Aspergillus and and Penicillium were the dominant fungal genera in the bioaerosol samples. Some pathogenic microbes, such as Arthrobacter, Bacillus, Arthrobotrys and Aspergillus, high bioaerosol aerosolization capacities. have aeruginosa, Stenotrophomonas Pseudomonas maltophilia and Escherichia coli were the dominant pathogenic bacteria in the bioaerosols formed during the landfill mining process, and microorganisms carrying VFGs in bioaerosol samples can spread VFGs

and aggravate the pathogenicity of bioaerosols. Therefore, more attention should be given to the prevention and control of bioaerosol pollution during landfill mining.

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## RISK ASSESSMENT OF LONG-TERM LEACHING OF HEAVY METALS FROM SOLIDIFIED/STABILIZED MSWI FLY ASH COUPLED LANDFILL DISPOSAL UNDER FREEZE-THAW AND DRY-WET CYCLES

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### ABSTRACT

The growth in municipal solid waste incineration (MSWI) has resulted in a substantial rise in the production of fly ash (FA) in China. It is anticipated that during the "14th Five-Year Plan", the accumulated amount of FA stocked and disposed of at landfills will surpass 100 million tons. Solidification/stabilization pre-treatment coupled with landfill disposal is the mainstream method for FA. However, in the long-term landfill process of solidified/stabilized (S/S) FA, natural environmental factors will affect the changes of its matrix (mineral structure and binder chemical properties), increasing the leaching risk of heavy metals. Therefore, in this study, the heavy metals (Pb, Zn, Cu, Cr, Cd, Ni) leaching properties and risk assessment of two representative S/S FA matrices, i.e., sodium dithiocarbamate (SDD) chelator treated and Portland cement + SDD combining treated, were evaluated by long-term freeze-thaw (F-T) and dry-wet (D-W) cycles assessment method. In addition, the effect of carbonization on heavy metals leaching under F-T and D-W conditions was explored through the design of carbonization experiments. The results showed that compared with F-T cycles, D-W erosion had a significant deterioration effect on the S/S FA matrix and increased the heavy metals leaching risk. Furthermore, carbonization promoted heavy metal leaching under F-T cycles, but to some extent inhibits heavy metal leaching under D-W cycles. The research results can provide scientific basis and theoretical reference for risk control and S/S technology selection of FA landfill sites in China.

### **KEYWORDS**

fly ash, freeze-thaw cycles, dry-wet cycles, heavy metals, carbonization

### INTRODUCTION

With the increasing amount of municipal solid waste (MSW), incineration has become the most common method of treating MSW in large and medium-sized cities in China, due to its advantages of reducing the volume of MSW by 80–90% and the mass by 75 %, completely eliminating pathogens and recovering energy [1-3]. MSWI FA as a secondary pollutant of incineration technology, is classified as HW18 hazardous waste in China due to the presence of toxic heavy metals and toxic organic compounds (e.g., dioxins, furans). Currently, 90% of FA is disposed of by solidification/stabilization (S/S) pre-treatment coupled with landfill disposal, which includes adding binders and/or chemical additives to S/S FA [4]. However, the practicality and short-term effectiveness

of S/S technique has been placed more emphatic, whereas long-term effectiveness and sustainability concerns are often overlooked. In the realistic disposal scenario of FA, due to landfill sequences, management operations, and other reasons, there will be phenomena such as stored in the open for an extended period of time prior to landfilling or co-landfill with MSW, and the process is susceptible to the negative impacts from the external environment (meteorological factors, leachate and acid rain erosion, carbonation, etc.) to make the S/S FA aged (Fig. 1) [5-7]. However, the multifaceted environmental impacts and physical factors (e.g., temperature, freeze-thawing, moisture, pore structure) are overlooked, which could cause adverse defects in the S/S FA and increase the risk of heavy metals secondary release. Wang et al. [8] investigated the impact of multiple environmental stresses (freeze-thaw+dry-wet+accelerated carbonation) on the aging of S/S FA and found that the degree of deterioration increased with cycling.



Fig. 1. Schematic illustration of environmental factors affecting the leaching of S/S FA in realistic landfill disposal scenario.

The objectives of this work are to: (1) prepare SDD chelator and OPC+SDD FA specimens; (2) evaluate the physical and chemical leaching performance of these specimens during accelerated aging process under freeze-thaw (F-T) and dry-wet (D-W) cycles, including moisture content, pH, acid neutralization ability (ANC) and heavy metal leaching concentration; (3) explore the effects of carbonization on the physical and chemical characteristics of S/S fly ash samples under F-T and D-W cycles by setting up polyvinyl alcohol membrane (PVA) covered and non-PVA covered groups. These data were provided with the risk control and management methods for heavy metals in the S/S treatment and final disposal process of FA.

# MATERIALS AND METHODS

### **Experimental samples and chemical reagents**

The MSWI FA samples were collected from the grate furnace MSWI plant, which is located in Qingdao, Shandong Province, China. The PO 32.5 cement was used in this study. The element composition of the FA and OPC cement was tabulated in Table 1. Sodium dithiocarbamate (SDD) commercial chelating agent was supplied by the Macklin.

Table 1 Contents of the chemical components and heavy metals in FA and OPC.

| Chemical                       | Contents (%) |        | Heavy  | Content (mg/kg) |  |
|--------------------------------|--------------|--------|--------|-----------------|--|
| Components                     | MSWI FA      | Cement | metals | MSWI FA         |  |
| Cl                             | 21.64        | _      | Zn     | 4054.25±45.61   |  |
| SO3                            | 9.24         | 4.39   | Pb     | 939.75±13.79    |  |
| CaO                            | 44.69        | 34.22  | Cu     | 393.55±11.81    |  |
| SiO <sub>2</sub>               | 2.33         | 32.47  | Cr     | 60.10±5.09      |  |
| Al <sub>2</sub> O <sub>3</sub> | 0.77         | 20.07  | Cd     | 160.55±2.26     |  |
| MgO                            | 1.44         | 3.85   | Ni     | 23.20±3.61      |  |
| Fe <sub>2</sub> O <sub>3</sub> | 0.88         | 2.34   | Hg     | 31.95±9.19      |  |
| TiO <sub>2</sub>               | 0.20         | 0.87   |        |                 |  |
| Na <sub>2</sub> O              | 10.15        | 0.62   |        |                 |  |
| K <sub>2</sub> O               | 7.62         | 0.71   |        |                 |  |
| ZnO                            | 0.57         | 0.01   |        |                 |  |
| CuO                            | 0.07         | 0.01   |        |                 |  |
| PbO                            | 0.17         |        |        |                 |  |
| Cr <sub>2</sub> O <sub>3</sub> | 0.04         | 0.03   |        |                 |  |
| MnO                            | 0.04         | 0.10   |        |                 |  |

#### Preparation of specimens of MSWI FA

The experimental samples included stabilized FA and

solidified/stabilized FA were obtained by stabilizing raw FA with 4% SDD and 7% OPC + 4% SDD, respectively. Distilled water was used in this experiment. The SDD commercial chelating agent was slightly diluted by distilled water for stirring more evenly. The moisture content of experimental samples was maintained about  $27\%\pm2\%$ . The homogenized experimental samples were dried in room temperature for 48 h. The mineralogy of experimental samples were analyzed using X-ray powder diffraction (XRD) and the results are shown in Fig. 2.



Fig. 2. XRD pattern image of raw FA, and SDD FA and OPC+SDD FA samples.

### Freeze-thaw, dry-wet cycles and carbonization tests

F-T and D-W are typical climatic conditions in northern and central China, respectively. Based on the meteorological characteristics in the actual FA landfill sites, the long-term cycle assessment method was set up as shown in Table 2, and the long-term cycle was conducted under the set experimental conditions. In addition, carbonization experiments were conducted using the moisture permeability and air resistance properties of PVA membrane, and SDD FA and OPC+SDD FA samples covered with PVA membrane were set up.

Table 2 Experimental conditions for F-T, D-W, and NC

| Experimental           | Temperature(°C)     |      | Time (h)  |      |                     |     |          |  |  |  |  |  |
|------------------------|---------------------|------|-----------|------|---------------------|-----|----------|--|--|--|--|--|
| condition              | Freeze              | Thaw | Freeze    | Thaw |                     |     |          |  |  |  |  |  |
| F-T cycles             | -30                 | 30   | 8.5       | 15.5 |                     |     |          |  |  |  |  |  |
| Experimental           | Temperature(°C)     |      | Time (h)  |      | Humidity            |     | Wet      |  |  |  |  |  |
| condition              | Dry                 | Wet  | Dry       | Wet  | Dry                 | Wet | moisture |  |  |  |  |  |
| D-W cycles             | 30                  | 25   | 17        | 7    | /                   | 60% | 45%      |  |  |  |  |  |
| Experimental condition | Temperature(°C)     |      | Time (h)  |      | Humidity            |     |          |  |  |  |  |  |
| Natural<br>control     | Room<br>temperature |      | Continued |      | Natural<br>humidity |     |          |  |  |  |  |  |

### **Analytical procedures**

During the long-term tests, the pH of the SDD FA and OPC+SDD FA were measured using a pH meter (PHS-3C; Shanghai INESA, China). Heavy metals concentration in the sample was determined by using inductively coupled plasma optical emission

spectrometry (ICP-OES; Agilent 5100; Agilent Technologies, USA). To determine the heavy metals content in the sample, the FA samples were digested using a HNO<sub>3</sub>/HCl/HF mixture by a microwave digestion system (XT9912; Xintuo Co., Ltd., China), and then analyzed by ICP-OES (Li et al., 2019; Wang et al., 2018b). A 2g sample was placed into a 50 mL centrifuge tube. Then, based on a liquid-solid (L/S) ratio of 10:1 L/kg, a certain volume of 5 M HNO<sub>3</sub> solution was added to the tube every 1 h. After rotating at 50 rpm for 1 h, centrifugation was performed and the pH value of the supernatant was analyzed to determine ANC.

### **RESULTS AND DISCUSSION**

#### Freeze-thaw cycles

Variation of moisture content and pH:

Fig.3(a) shows that the overall trend of moisture content in each FA sample during F-T group is similar, showing an upward trend. As of the 80th cycle, the moisture content reached as high as 45.22%-47.04%, while the NC group shows a gradually downward trend. Except for the non-PVA covered FA samples of NC, the pH showed a slow decreasing trend under F-T and NC groups. However, from the 60th to the 80th cycle, the SDD FA and OPC+SDD FA rapidly decreased from 12.07 and 12.15 to 8.88 and 9.03, respectively. This shows that PVA membrane have a good resistance to carbonization.



Fig. 3. The changes in (a) moisture content and (b) pH of different FA samples under F-T and NC groupss.

### Variation of acid neutralization ability:

A comparison of the ANC of F-T and NC groups FA samples at different periods is shown in Fig. 5. Within cycles 1 to 5, the ANC of each FA sample has been enhanced, possibly due to the ongoing development of the solidification/stabilization effects of OPC and SDD on FA. However, from the 10th cycle onwards, the ANC of the F-T and NC groups decreased significantly, with the NC group showing a greater reduction in ANC compared to the F-T group.



Fig. 4. Acid neutralization capacity of different FA samples under F-T and NC groups.

Leaching behavior of heavy metals:

Fig. 5 shows the leaching concentration changes of heavy metals in stabilized FA and solidified/stabilized FA during aging. The heavy metal leaching concentrations did not exceed the limits (GB 16889-2024) under both F-T and NC groups up to 80 cycles. However, it is noteworthy that Pb and Cd still pose a significant leaching risk under continued aging, in agreement with the ANC, most of the heavy metals were leached at higher concentrations under the NC than under the F-T group.



Fig. 5. Leaching behavior of heavy metals in different FA samples under F-T and NC groups.

### Dry-wet cycles

Variation of pH:

Fig. 6 shows the pH changes of each FA sample during 60 cycles of D-W and NC groups. It can be clearly found that the effect of dry and wet on the pH of FA

matrix is more significant than that of F-T and NC. During the 0-60 cycles, the pH of the non-PVA covered SDD FA and OPC+SDD FA groups decreased from 12.67 and 12.66 to 8.01 and 8.08, respectively, while that of the PVA covered SDD FA and OPC+SDD FA groups decreased from 12.66 and 12.68 to 8.21 and 8.29, respectively.



Fig. 6. The changes in the pH of different FA samples under D-W and NC groups.

Variation of ANC:

The ANC of each FA under D-W group decreased to varying degrees with time, and from 5th cycle onwards, the ANC capacity of FA under alternating dry and wet conditions decreased significantly, especially in the non-PVA covered group, and the difference in ANC between D-W and NC group gradually increased. This is mainly due to the higher moisture content of FA samples under wet conditions, which can easily react with  $CO_2$  in the air to cause carbonization. In addition, the ANC was similar over time, despite the difference in pH between the non-PVA and PVA covered groups.



Fig. 7. Acid neutralization capacity of different FA samples under D-W and NC groups.

Leaching behavior of heavy metals:

Fig. 8 shows the leaching concentration changes of heavy metals in stabilized FA and solidified/stabilized FA during aging. The most heavy metals leaching concentration under D-W group is higher than that of the NC and F-T groups. Combined with the ANC analysis in Fig. 6, it was found that heavy metals in the samples under D-W group also showed a significant increase in leaching from the 5th cycle. At the 35th cycle, the leaching risk of heavy metals other than Pb and Cd is relatively low. In the non-PVA covered group, the release of Pb and Cd in the stabilized FA exceeded the landfill site limit value in the 25th cycle, while the release of Pb and Cd in the solidified/stabilized FA exceeded the limit value in the 35th and 30th cycles, respectively. It can be seen that addition cement can effectively control the long-term leaching risk of heavy metals to some extent.



Fig. 8. Leaching behavior of heavy metals in different FA samples under D-W and NC groups.

### CONCLUSIONS

This study combines physico-chemical properties, ANC, and heavy metal leaching results to analyze the long-term leaching risk of stabilized and solidified/stabilized FA matrix under F-T, D-W and NC groups. The conclusions are as follows:

1. Compared with F-T and NC groups, D-W group have the greatest effect on the pH of SDD FA and OPC+SDD FA matrix, which decreased from 12 to around 8 by the 60th cycle.

2. In the actual landfill process, the solidified/stabilized FA covered with PVA can effectively prevent the leaching of heavy metals under freeze-thaw conditions after entering the landfill. However, in the D-W conditions, membrane covering has a negative affect on the leaching of heavy metals in solidified/stabilized FA; 3. The pre-treatment method of FA in F-T environment has little effect on heavy metal leaching, but the addition of cement in the early stage of D-W group can effectively control the long-term leaching risk of heavy metals to some extent.

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# Thorough analysis of rare earth element distribution in landfill soils and implications for REE extractability

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### ABSTRACT

The escalating global demand for rare earth elements (REEs) necessitates the development of sustainable resource recovery strategies. This study conducts a comprehensive analysis of the presence of REEs in landfill humus soil. Concentrations of REEs varied from 146 to 464 mg/kg, influenced by landfill parameters and deposition of industrial waste. Utilizing the Tessier extraction method, it was found that most REEs reside in unextractable residual fractions, such as phosphates, highlighting their high stability and strong binding to soil components. Additionally, significant variation was observed across different soil particle sizes, with finer soil fractions accumulating higher concentrations of REEs. This study enhances the understanding of REE distribution in landfill soil and identifies landfill soil as a viable source for critical metal recovery.

### **INTRODUCTION**

Global population growth, technological advancements, and increased economic activities are driving the rapid development of clean energy, communication, and transportation products, which consume vast quantities of rare earth elements (REEs) (Goodenough et al., 2018). REEs, comprising 17 elements including the 15 lanthanides, yttrium, and scandium, are essential for everyday applications and industrial processes, making them highly competitive in the global market (Gong and Xu, 2022). However, continuous virgin mining has caused significant environmental damage (Karna et al., 2017), and geopolitical tensions have led to export restrictions, raising supply concerns (Gao et al., 2024). Consequently, governments are seeking alternative REE sources from waste materials (Vivoda, 2023).

Utilizing waste by-products offers substantial economic and environmental benefits globally (Gupta et al., 2024). Industrial by-products like coal fly ash and phosphogypsum, along with electronic waste (E-waste), contain significant levels of REEs (Gaustad et al., 2021). Traditionally, industrial waste and E-waste have been disposed of in landfills, often after incineration (Kayla Kilgo et al., 2022). Recent studies have identified high concentrations of REE in landfill bottom ash, recognizing landfills as substantial reservoirs of secondary resources (Beikmohammadi et al., 2023).

Landfill soil, comprising 50%~60% of landfill content, is a significant accumulator of REEs due to its mineral and humic acid composition, high surface-to-volume ratio, and rich organic matter, which enhance cation exchange and adsorption (Xiao et al., 2022). Despite its potential, the resource value of landfill soil is underexplored, with previous studies focusing on heavy metals and overlooking REEs (Burlakovs et al., 2018; Hölzle et al., 2022). This study investigates the presence, speciation, and abundance of REEs in soil from 11 Chinese landfills, including 14 units from Shanghai Laogang Landfill (1990-2013), and explores their correlation with soil characteristics and urban development. Additionally, it evaluates the occurrence of REEs, exploring the possibility of resource recycling.

### MATERIALS AND METHODS Study area and sampling

This study involved sampling residual waste from 11 landfills across various regions of China: Dongguan (D), Xiamen (X), Wenzhou (W1), Fuzhou (F), Quanzhou (Q), and Shanghai in the south; Wuhan (W2) and Lixin (L1) in the central region; and Harbin (H), Jiamusi (J), and Langfang (L2) in the north. Aged landfills that had reached the stabilization stage were selected, and a grid-based sampling method was employed using a drilling machine. The general information of the study areas is shown in **Figure 1**.



Figure 1. General locations of the landfills studied (a); Satellite image of Shanghai Laogang Landfill, with
units outlined in the white frame (b); Structure of the Shanghai Laogang Landfill, with selected units marked by stars (c).

Figure 1 (a) displays the approximate locations of the landfills in different cities. Figure 1 (b)(c) highlight the Shanghai Laogang Landfill, the largest landfill in Asia, comprising 57 units, of which 14 units were sampled. Waste samples from each collection were categorized into four main components: soil, inorganic aggregates, plastics, and fabrics. Separated soil was dried in an oven at 80°C and then sieved using stainless steel mesh screens of three sizes, separating the soil into four fractions: <75  $\mu$ m, 75~150  $\mu$ m, 150~270  $\mu$ m, and >270  $\mu$ m.

#### Chemical analysis

Characteristics of preprocessed soil samples, including pH, cation exchange capacity (CEC), and organic matter (OM), were measured according to relative standards (HJ 962-2018, HJ 889-2017, and HJ 761-2015) (Ministry of Ecology and Environment People's Republic of China, 2018, 2017, 2015). A 3 g sample of dried landfill soil was placed into a 50 mL centrifuge tube, and sequential extraction of REEs was performed in four steps, using the Tessier method (Tessier et al., 1979). The REEs were separated into four fractions: exchangeable, Fe-Mn oxide-bound, organic-bound, and residual fractions. Residues after each step were characterized and observed using X-ray diffraction (XRD, Bruker D8 ADVANCE Diffractometer) and scanning electron microscope (SEM, FEI NOVA 450). The residual fraction was digested on a graphite heating plate at 180 °C for 2 hours using a mixture of concentrated HNO<sub>3</sub>, HF, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub> (GR, Sinopharm) to dissolve silicate, phosphates, and fluorides. The solutions from the four fractions were diluted to a final volume of 50 mL, and the REEs were quantified using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700). Quality assurance and control (QA/QC) measures were ensured using reagent blanks, duplicate samples, and reference materials for REEs. standard The concentration of elements, relative abundance of different elements, distribution among the four fractions, and particle sizes were analyzed to assess REEs' content in soil.

#### **Correlation analysis**

To investigate the external factors that influence the heterogeneous distribution of REEs in landfills, additional analysis was conducted using correlation coefficient to assess relationships among variables. The concentrations of REEs were used as the dependent variables. The independent variables were categorized into four groups: industry, waste, human activity, and physicochemical properties in soil. Ten factors from these categories were identified potentially related to REE concentration in landfills and were applied as independent variables in this study.

In the 'Industry' category, industrial output-especially in the electronics and communications (TIO and OVEMI)-was considered, as it represents a significant portion of REE-containing products. Coal consumption (CC) was also factored in, as it correlates with the production of coal ash. In the 'Waste' category, unrecycled or non-reused industrial waste (ISWD) was considered, as it typically ends up in landfills. The landfill's age (Years) and depth (Depth) were also included, as they influence potential for waste components to migrate over time. The permanent resident population (PRP) was included as a factor influencing the scale of industry and waste generation. Furthermore, the physicochemical properties of soil-pH, CEC, and OM-were regarded as critical to the soil's ability of adsorption and complexation (Dinali et al., 2019).

Spearman correlation analysis was widely applied to evaluate the strength, direction, and significance of the relationships between variables (Tosepu et al., 2020; Yuan et al., 2024). This method is particularly useful when dealing with ordinal data or when the assumption of normality and homoscedasticity are not met (Schober et al., 2018). The analysis focused on the correlation coefficient ( $\rho$ ) and the significance level (p-value), calculated as:

$$d_i = Rank(X_i) - Rank(Y_i)$$
(1)

$$\rho = 1 - \frac{6\sum d_i^2}{n(n^2 - 1)}$$
(2)

$$p\text{-value} = \rho \sqrt{\frac{n-2}{1-\rho^2}} \tag{3}$$

Where di is the difference between the ranks of the *i-th* data in the two variables, n is the number of data points. The correlation coefficient  $\rho$  quantifies the strength and direction of the association between variables, ranging from -1 (strong negative correlation) to 1 (strong positive correlation). The significance level (*p*-value) helps determine whether the observed relationship is statistically meaningful or due to chance.

#### **RESULTS AND DISCUSSION REE distribution in landfill soil**

The descriptive statistical characteristics of REE concentration in soil from the landfills studied are presented in **Figure 2**. In **Figure 2** (a), total REE concentrations ranged from 146 to 381 mg/kg, with

most exceeding the Chinese soil background value (181 mg/kg), except for the Fuzhou and Langfang landfills (Hu et al., 2006; Zhang and Shan, 2001). This indicates that REEs accumulate in soil as landfills stabilize. The lowest concentration was recorded in the Fuzhou landfill, while the highest was in the Dongguan landfill. The total REE concentration in Dongguan was comparable to that of coal fly ash (300~1500 mg/kg) which was a recognized secondary REE resource, indicating that soil in some landfills may serve as a potential resource for REE recovery (El-Fadel et al., 1997; Fritz et al., 2023). Other landfills, such as those in Xiamen, Wenzhou, and Quanzhou, exhibited total REE concentrations in the range of 200~300 mg/kg.



Figure 2. Total REE concentrations and their relative proportions in landfills across different cities (a), and units of Shanghai Laogang Landfill (b), with dash line representing soil background concentration in China.

The relative concentrations of individual REEs, as shown in Figure 2 (a), indicated that Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Gadolinium (Gd), Scandium (Sc), and Yttrium (Y) were the dominant components in most landfills, contributing 12.59%~15.74%, 33.10%~63.50%, 1.80%~7.72%, 8.45%~22.89%, 1.45%~3.50%, 2.17%~5.56%, 1.27%~4.90%, and 2.55%~9.80% of the total REE content, respectively. Ce consistently emerged as the most abundant element. In the Xiamen and Wuhan landfills, Europium (Eu) accounted for 8.80% and 14.66% of the total REE content, while in other landfills, Eu's contribution

remained below 3%. On average, Dysprosium (Dy), Holmium (Ho), Erbium (Er), Ytterbium (Yb), and Lutetium (Lu) occupied 0.52%~1.57% of the total REE content. Notably, Terbium (Tb) and Thulium (Tm) were not detected in any of the samples.

Figure 2 (b) illustrates the total REE concentrations and relative abundances in soil from the Shanghai Laogang Landfill. Unit 8 displayed the highest REE concentration, reaching 464 mg/kg, making it the richest among all samples. In contrast, unit 14 had the lowest concentration of REEs at 183 mg/kg. Other units exhibited REE concentrations ranging from 211 to 340 mg/kg, highlighting significant year-to-year variations in discarded secondary resources and released elements, even within the same city.

The relative abundance of REEs also varied among units in the Laogang Landfill. La, Ce, Pr, Nd, Sm, Eu, occupied 8.98%~15.93%, Gd, Sc. and Y 17.69%~52.97%, 0.18%~38.84%, 5.28%~27.26%, 0~4.11%, 0.03%~2.80%, 3.03%~5.56%, 1.22%~3.67%, and 2.44%~7.34%, respectively, across the 14 units. Although Ce remained the dominant REE in most units, Pr concentrations exceeded those of Ce in units 4, 6, 9, 10, and 11.

When considering all 11 landfills together, light REEs (La to Gd) (Borst et al., 2020; Weng et al., 2015), accounted for the majority of total REE content in soil. In contrast, heavy REEs (Sc, Y and Tb to Lu) were present in relatively lower concentrations. This distribution pattern aligns with findings from coal ash studies, which also report higher accumulation of light REEs compared to heavy REEs (Park et al., 2021). This trend reflects the broader distribution and more frequent use of light REEs, leading to their higher accumulation in comparison to heavy REEs (Weng et al., 2015).



Figure 3. Proportion of various forms of major REEs in landfills (a); Distribution of major REEs across four particle size fractions (b).

**Figure 3 (a)** presents a comparative analysis of the fractional distribution of major REEs—La, Ce, Pr, Nd, Sm and Y—across different samples. On average, the exchangeable fraction of these six elements accounted for 6.31%~9.15% of the total concentration, with Pr being the most widely dispersed between 0% and 24.96%. The Fe-Mn oxide-bound and organic matter-bound fractions collectively contributed no more than 15% of the total REE content. The majority of REEs were found in the residual fraction, making up

58.48%~99.49% of the total content, indicating their association with more stable mineral phases. Notably, the interquartile range of residual Nd was broader than that of others, suggesting a greater degree of variation in Nd content across different soil samples. These findings suggested that REEs could be held by electrostatic forces on organic matter and exchangeable, while the majority of REEs in landfill soil were stable and immobile, which aligned with studies by Lin et al. and Hu et al., who reported similar REE stability in coal fly ash and various soils types (Hu et al., 2006; Lin et al., 2018).

**Figure 3 (b)** shows the distribution of REEs across different particle sizes of soil. The highest proportion of major REEs was primarily concentrated in particles smaller than 75  $\mu$ m, with an average of 40.20% for La, 40.40% for Ce, 39.60% for Pr, 39.39% for Nd, 36.44% for Sm, and 37.32% for Y. Among larger particle sizes, distribution of REEs showed little difference. Overall, smaller soil particles were more conducive to REE accumulation, consistent with previous research (Valentim et al., 2019). This could be attributed to the higher surface area-to-volume ratio and greater number of sorption sites in smaller particles, which enhances their adsorption capacity for REEs (Han et al., 2022).

The mineralogical composition and the appearance of landfill soil were investigated using XRD and SEM-EDS (**Figure 4**). Crystalline phases identified included quartz (SiO<sub>2</sub>) and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), which remained typical and stable after sequential extraction. SEM analysis revealed varying soil morphologies across 3 steps. Surface adherence of soluble microparticles was progressively removed, leading to a predominant presence of silicon and aluminum oxides. Elemental scanning detected fine particles of yttrium phosphate embedded within the anorthite phase, suggesting that REEs may existed as independent phases and are adsorbed by soil minerals.



Figure 4. XRD and SEM-EDS analysis of landfill soil

before and after each sequential chemical extraction step.

#### Potential distributors on REE concentration

To estimate REE content in additional landfills, factors that may influence REE concentrations were evaluated using Spearman correlation coefficients, as shown in Figure 5 (a). Most selected factors showed a positive correlation with REEs, except for CEC, which negatively correlated with REE concentrations. OM had highly significant correlation with REEs а (p-value<0.001), while Years and industrial solid waste disposal (ISWD) showed strong correlations with REEs (p-value<0.01). This phenomenon indicated that other than mineral phase, organic matter in soil may also be an adsorbent of REEs. Other factors such as PRP, total industrial output (TIO), CC, output value of electronics manufacturing industry (OVEMI), and Depth were also associated with REE concentrations to varying extents. These findings suggest that high organic matter content, longer landfill ages, and increased industrial waste disposal are linked to higher REE concentrations.



Figure 5. Ranking of variables based on Spearman correlation with total REE concentration (a); Scatter plots with linear regression fits for significant factors affecting REE concentrations (b-d); Spearman Correlation coefficients between variables (e).

Despite these correlations, Figure 5 (b-d) illustrates that although positive influences between factors and responses could be predicted, no single factor could fully explain REE concentrations through a linear fit, suggesting that a combination of variables must be considered. To fully understand the complex relationships between multiple factors and REE concentrations, further data collection and analysis are needed to build a more comprehensive analysis system. The correlations between different factors are shown in Figure 5 (e), with red indicating positive correlations and blue indicating negative correlations. TIO, PRP, CC, and OVEMI were strongly correlated, reflecting the interconnection of these factors. The electronics manufacturing industry plays a significant role in TIO, and coal provides power and energy to support industry. Resident population influences local industry by supplying labor and driving demand for industrial products and electricity. Additionally, the positive correlation between landfill age and the proportion of disposed waste is explained by the lack of strict recycling regulations in earlier years, which resulted in large amounts of industrial solid waste being landfilled.

#### CONCLUSION

This study comprehensively discovered the presence, speciation, and economic potential of REEs in landfill soil across China. The findings reveal that concentrations of REEs in landfill are comparable or even higher than some secondary or primary resources like coal ash and minerals. Most REEs are predominantly found as residual fraction, indicating their high stability and strong binding to humic acid component. Phosphate is a vital carrier for REEs, which is independent from primary soil structure. Key factors influencing REE accumulation were pinpointed, including organic matter in soil, industrial waste disposal, and landfill age.

This research highlights a previously underexplored resource that could alleviate REE supply constraints. Future research should validate these findings across diverse global backgrounds and landfill types. Also, efficient supply chains and recovery methods should be specially designed to support a robust and well-developed market.

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### **Smart Sorting Technologies for Food Waste Management**

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#### Abstract

Effective food waste processing is essential for advancing environmental conservation and resource recovery, yet improper sorting frequently results in the contamination of food waste with inorganic waste. This contamination negatively impacts the operational efficiency of food waste treatment facilities, where preliminary sorting often depends on labor-intensive processes. To address the challenge of a nonhomogeneous food-inorganic waste stream, this study proposes a vision-based system for effective sorting. A Mixed Food-Inorganic Waste (MFIW) dataset, comprising over 13,000 samples across four distinct inorganic waste categories, was developed. Based on dataset analysis, a waste detection model employing Deformable Convolution v3 and tailored positioning and classification algorithms was implemented to enhance detection performance. This model achieves an mAP<sup>50</sup> of 85.21%, with average recalls surpassing 94% for packages, trash bags, and animal bones, operating at a real-time rate of 33.61 FPS, underscoring its robustness for industrial deployment.

#### 1. Introduction

Global urbanization, population growth, and economic development have significantly increased municipal solid waste (MSW) generation (Chen et al., 2020; Karak et al., 2012) . Annually, the world produces around 2.01 billion tons of MSW, with food waste (FW) comprising about 64% of total waste in developing countries (Gautam & Agrawal, 2021; Y. Wang et al., 2023). FW disposal through incineration and landfilling is economically damaging and emits approximately 4.4 gigatons of greenhouse gases annually (Jaglo et al., 2021). Proposed solutions include management policy development, resource recycling promotion, efficient technology advancement, and raising public environmental awareness (Ambaye et al., 2023; Iyamu et al., 2020; Nanda & Berruti, 2021; Shah et al., 2021). The effectiveness of FW management measures often depends on a country's development level and regulatory enforcement challenges. These nations often face operational skill limitations, funding shortages, and insufficient maintenance and management practices, hindering effective waste sorting. Consequently, the FW is mixed with a large amount of inorganic waste (Nizami et al., 2017; Secondi et al., 2015; Torres-León et al., 2018). This has significantly increased the burden on end-of-pipe FW management, making the efficiency

greatly reduced (Alwi et al., 2016; Palomar et al., 2019; Zotter, 2004) . Additionally, the reliance on manual labor for waste sorting exposes workers to health and safety risks (Lee et al., 2017; Y. Wang et al., 2022) . Adopting Industry 4.0 and Circular Economy principles can help address this challenge by developing intelligent sorting systems capable of autonomously categorizing materials, thus enabling new methods of waste valorization (Konstantinidis et al., 2023a).

Advances in artificial intelligence and computational capabilities have increased research interest in intelligent waste sorting. Computer Vision (CV) neural networks, particularly when integrated with robotics or automation, demonstrate high accuracy in waste sorting after training on various datasets (Lu & Chen, 2022). Early waste sorting studies focused on simple classification tasks, where waste items moved through the camera's view sequentially on conveyor belts, without needing precise positioning. Recently, convolutional and attention-based neural networks inspired by the TrashNet dataset have reached high accuracy, with one study achieving 99.60% (Mao et al., 2021; Rabano et al., 2018; M. Yang & Thung, 2016; Z. Yang & Li, 2020). However, classification approaches are insufficient for continuous waste streams in industrial settings. Researchers are increasingly recognizing these limitations, focusing on detectionbased systems that can identify multiple waste items in a single frame. Detection-based sorting considers both material type and the exact position and contours of each item (Ku et al., 2021). Real-world waste streams on conveyor belts are densely packed with overlapping materials, making detection more complex than basic classification tasks. To address this, the Trash Annotation in Context (TACO) dataset was developed, providing 1,500 images across 28 household and municipal waste categories for training detection models (Proença & Simões, 2020). Since then, many waste detection datasets covering domestic, industrial, and aquatic waste have been developed, and studies using both public and proprietary datasets show strong performance (Konstantinidis et al., 2023b; Koskinopoulou et al., 2021; Panwar et al., 2020).

Although these studies show high performance in waste sorting, few focus on FW sorting. Additionally, no dataset has yet been developed for food-inorganic waste sorting in industrial settings. Moreover, separating inorganic waste from FW presents greater challenges than conventional waste sorting tasks. Unlike the homogeneous waste streams seen in other sorting tasks, FW accumulates, often covering or contaminating inorganic waste. This accumulation complicates the detection of inorganic waste by vision-based models.

To address these challenges in food-inorganic waste sorting, this study developed a vision-based sorting system. The primary contributions of this work are threefold. First, a real-world dataset named the Mixed Food-Inorganic Waste (MFIW) dataset was developed, containing over 13,000 samples across four common inorganic waste categories in food waste: packages, trash bags, bottles, and animal bones. Second, a waste detection model utilizing Deformable Convolution v3 (DCNv3) was implemented to sort inorganic waste from food waste (FW) streams (W. Wang et al., 2023a). By analyzing the MFIW dataset, the study optimized positioning and classification algorithms for enhanced detection performance, with transfer learning accelerating convergence and further boosting model accuracy. Finally, the DCNv3-based model surpassed both the Swin Transformer and YOLO-v8 models, achieving an mAP<sup>50</sup> of 85.21%, and classification accuracies above 94% for packages, trash bags, and animal bones (Jocher et al., n.d.; Liu et al., 2021). With a frame rate of 33.61 FPS, the model met real-time industrial requirements, demonstrating the feasibility of a vision-based system for food-inorganic waste sorting.

#### 2. Materials and Methods

A detailed description of the proposed vision-based sorting system is provided in **Figure 1** (a). The monitoring device sends real-time video to the detection model, which determines the position and classification of inorganic waste. Finally, the waste is sorted by the machinery. The materials and methods section will primarily cover the creation of the dataset and the selection of the detection model. In addition, the evaluation criteria of detection model will be discussed.



**Figure 1.** (a) Overview of the vision-based sorting system, comprising a monitoring device, detection model, and sorting machinery. (b) Example of labeled data: the input image size is set to  $n \times n$ , with inorganic waste samples selected, categorized, and labeled based on type and size. Coordinates *x*, *y* denote the upper left position, while *w* and *h* represent the length and width of each sample within the image.

#### 2.1 Dataset preparation

In this section, the MFIW dataset was created for model training. This dataset helps the detection model adapt to scenarios involving mixed food and inorganic waste sorting. Data on FW was obtained from a food waste treatment facility in Shanghai, which plays a pivotal role in managing kitchen waste for six districts in the city. For this research, a GoPro camera (Hero9 Black, GoPro Inc., US) was used to record a continuous video documenting the waste flow. The video footage was

then divided into individual images. In the constructed dataset, notable waste categories were identified and classified using the custom software LabelImg (available at https://github.com/HumanSignal/labelImg). An example of labeled data is shown in **Figure 1**. (b). The MFIW dataset was categorized into four types: package, trash bag, bottle, and animal bone. The detailed information is shown in the Table S1.

#### 2.2 Waste sorting model

The structure of the detection model primarily consists of three parts: backbone, neck, and head, as shown in **Figure 2**. The backbone is primarily responsible for image feature extraction. After the backbone extracts hierarchical features from the input data, the neck, situated between the backbone and the head, refines and fuses these features across different scales (Tan et al., 2020). This process enhances the ability of model to detect objects of varying sizes and shapes. This connection ensures that the detection head receives more informative and contextually rich features, which are crucial for accurate object detection. Finally, the positioning and classification algorithms are used to determine the location and category of waste (Lin et al., 2017; Zheng et al., 2020).



**Figure 2.** Framework of the waste sorting model. The backbone performs feature extraction at four distinct levels, then directs the extracted features into Neck for feature fusion. The integrated features are then fed into three dedicated heads responsible for the precise regression of the position and classification of waste.

In food waste sorting, using Deformable Convolutional Networks (DCNs) as the backbone instead of conventional CNNs or Transformers is advantageous due to the non-rigid nature of waste, which undergoes significant deformation during transportation and compression. DCNs are better suited to capture these deformations and non-rigid characteristics, offering superior feature extraction capabilities for such objects, thereby enhancing detection accuracy in waste detection tasks. In this study, deformable convolution v3 (DCNv3) was used as the core operator for the backbone (W. Wang et al., 2023b).

#### 2.3 Evaluation criteria

The performance of a sorting model goes beyond simple accuracy measurements. To comprehensively evaluate model outcomes and robustness, critical metrics such as Intersection over Union (IoU), precision, recall, average precision (AP), and mean average precision (mAP) must be considered. Object detection model predictions should be assessed on two fronts: positioning accuracy and classification accuracy. Positioning accuracy, illustrated in **Figure 3** (a), is determined using IoU.



Figure 3. (a) Definition of IoU. "Union" refers to the union of the predicted bounding box and the actual one, while "Overlap" refers to the intersection of the predicted and actual bounding boxes. (b) Simplified confusion matrix.

The alignment between predicted classification and the ground truth is crucial. A prediction is classified as a true positive (TP) when it meets the IoU threshold and corresponds with the correct ground truth classification. A prediction is a false positive (FP) if it doesn't meet these criteria. A true negative (TN) occurs when the prediction accurately identifies the absence of a ground truth object. Figure 3 (b) shows a simplified confusion matrix illustrating the relationships among TP, TN, and FP. Based on the confusion matrix, evaluation metrics like precision, recall, average precision, and mean average precision, used in this study, can be derived from equations (1) through (4):

$$Precision = \frac{TP}{TP+FP}$$
(4)

$$Recall = \frac{TP}{TP + FN}$$
(5)

$$AP = \int_0^1 Precision(R)dR \tag{6}$$

$$mAP = \frac{\sum_{i=1}^{C} AP_i}{c} \tag{7}$$

#### 3. Result and Discussion

Model training and evaluation were conducted in the PyTorch open-source deep-learning environment (developed by Facebook, Inc., CA, USA) using a graphics processing unit (NVIDIA GeForce RTX 4090, NVIDIA, Santa Clara, CA, USA). In this section, model training, positioning and classification performance, and industrial deployment will be discussed.

#### 3.1 Positioning performance

To evaluate the model's positioning performance, input signals with resolutions of 640x640 and 1280x1280 pixels were tested. The evaluation metrics included mAP<sup>50</sup> (IoU threshold of 0.5), mAP<sup>75</sup> (IoU threshold of 0.75), and mAP<sup>ave</sup> (the weighted average mAP from IoU 0.5 to 0.95).



Figure 4. (a) Comparison of positioning performance for different models. (b) Positioning performance of the Waste detection model in industrial scenario.

**Figure 4** (a) shows the comparative performance of different models, with the Waste Detection model outperforming both comparative models across all evaluation metrics. With a 1280x1280 pixel input, the Waste Detection model achieved an mAP<sup>50</sup> of 85.21%, outperforming the Swin Transformer by 12.71%. At an IoU threshold of 0.75, the mAP decreased to 66.67%. This reduction is acceptable given the difficulty of precisely outlining inorganic waste mixed with food waste due to irregular shapes, concealment, or contamination. With higher IoU thresholds, a further decline in mAP is observed, resulting in an mAP<sup>ave</sup> of 57.57%. When the input resolution was reduced to 640x640 pixels, the mAP<sup>50</sup> decreased to 77.20%, which remains acceptable for practical applications.

**Figure 4** (b) illustrates the model's positioning performance for mixed inorganic waste within the food waste (FW) stream in an industrial setting. Manually locating inorganic waste within food waste is generally infeasible, as inorganic waste is often mixed with or partially buried under FW, making manual sorting difficult. Fortunately, the Waste Detection model effectively outlines the boundaries of each inorganic waste category. This accuracy is noteworthy given the difficulty of identifying inorganic waste betection model's effective feature recognition in challenging scenarios demonstrates its superior capability to identify inorganic waste.

However, the accumulation of food waste decreases the accuracy of inorganic waste positioning. To prevent large accumulations, waste should be evenly distributed when placed on the conveyor belt. Furthermore, although the dataset includes over 13,000 samples, it remains insufficient for industrial application. The limited dataset also restricts the model's ability to accurately outline inorganic waste. Therefore, expanding the dataset in later research stages is essential.

#### **3.2** Classification performance

A Precision-Recall Analysis was conducted to evaluate the Waste Detection model's detection and classification efficacy for each inorganic waste category. The results are presented in **Figure 5** (a). The inverse relationship between precision and recall suggests that the area under the Precision-Recall curve reflects the model's accuracy. As shown in the figure, the Waste Detection model demonstrates higher accuracy across all analyzed inorganic waste categories compared to other models. This superiority is particularly notable in detecting packaging, trash bags, and bottles.



**Figure 5.** (a) Comparison of Precision-Recall curve across four categories for different models. (b) The Average Precision (AP) criteria for various categories identified by the Waste detection model. It provides insights into the classification performance of model. (c) The confusion matrix for the detection result. It offers a detailed analysis of the classification efficacy across different inorganic waste categories.

**Figure 5** (b) shows the detection accuracies of the Waste Detection model across different inorganic waste categories. The analysis reveals that the  $AP^{50}$  accuracy for each category exceeds 81%, while detection accuracies remain above 64% at the  $AP^{75}$  threshold. However, the  $AP^{50}$  value for animal bones is 81.81%, as their irregular shapes and lack of distinctive color features make it challenging for the model to generalize common characteristics during training. Consequently, animal bones show lower detection performance compared to other inorganic waste categories.

To further assess the Waste Detection model's classification accuracy for each category, a confusion matrix was generated, shown in **Figure 5** (c). A confusion matrix was computed for different inorganic waste categories to clarify classification performance. Each row of the confusion matrix corresponds to the

actual label of the dataset, while each column reflects the predictions of model. Acknowledging the complex background of FW stream, it is observed that certain amount of FW (background) is erroneously classified as inorganic waste. To address this discrepancy, an additional background determinant was added to the matrix. Analyzing the diagonal of the confusion matrix reveals that the model accurately recalls and categorizes over 94% of inorganic waste in the categories of packages, trash bags, and animal bones. However, 17% of positioned bottles were misclassified as packages. The misclassified samples are shown in Figure 6 (a). The reason for the misclassification is that the packaging on the surface of these bottles is identified as a package. Another reason is that the bottle is obscured by FW, making it appear more like a package than a bottle.



**Figure 6.** (a) Misclassified bottles by the Waste detection model. The packaging of the upper three bottles is obvious, and they are misclassified as packages; the lower three bottles obscured by food waste, making them misclassified as packages. (b) Deployment test of the Waste detection model.

#### 3.3 Model deployment

Further exploration is required to assess the practical applicability of the Waste Detection model for industrial applications. In this study, the TensorRT inference optimization tool (available at https://github.com/NVIDIA/TensorRT) was used for model deployment. This tool optimizes the model by using operator fusion and model quantization, which significantly enhance the Frames Per Second (FPS) rate during deployment. The accuracy performance (mAP<sup>50</sup>) and FPS after model compression are shown in Figure 6 (b). During the evaluation the Frames Per Second (FPS), input signal with varying resolutions, ranging from 320 to 1280 pixels, were employed. A reduction in the pixel count of the input signal inherently limits the ability of model to extract features, which in turn impacts the detection accuracy. At the same time, a reduction in resolution entails a decline in computational complexity, which speeds up the inference time per data frame. Since there is an inverse relationship between inference time and FPS, a negative correlation is observed between the FPS and the accuracy of model.

When the resolution of the input signal is reduced from 1280 to 640 pixel, the mAP<sup>50</sup> value of the model decreases from 0.852 to 0.772, which is deemed acceptable. This reduction is accompanied by a notable decrease in the mean inference time and a corresponding increase in the Frames Per Second (FPS), which rises from 17.16 to 33.61. However, at resolutions lower than 640 pixels, there is a significant decline in the mAP<sup>50</sup> value, falling below 0.70 when the resolution is further reduced to 480 pixels. These results suggest that, for industrial applications, the input resolution can be adjusted to balance the detection accuracy and FPS.

#### 4. Conclusion

This study presents a vision-based sorting system for positioning and classifying inorganic waste within the FW stream. The proposed technique addresses the issue of inorganic waste mixed with food waste affecting the regeneration process and enhances inorganic waste resource utilization. In the sorting system, a GoPro camera was used for real-time monitoring, and a DCNv3-based model was implemented for detecting inorganic waste. To enhance detection efficiency and accuracy, a custom MFIW dataset was created to help the detection model adapt to mixed food-inorganic waste sorting scenarios. The MFIW dataset consists of over 13,000 inorganic waste items across four categories: package, trash bag, bottle, and animal bone. In addition, transfer learning method was employed to accelerate convergence and improve detection accuracy. The Waste Detection model demonstrates excellent positioning and classification performance for inorganic waste. With a 1280x1280 pixel input, it achieved an mAP<sup>50</sup> of 85.21%, precisely outlining the boundaries of inorganic waste even when contaminated or partially buried in FW. At the same time, the detection accuracy of the model for each category of inorganic waste has reached an AP<sup>50</sup> criteria over 81%. The average recall for packages, trash bags, and animal bones exceeded 94%. Finally, model deployment results show that the Waste Detection model achieves a real-time FPS of 33.61 at an input resolution of 640 pixels.

designed system, despite the The outstanding positioning and classification accuracy for inorganic waste, also has some limitations. Firstly, in industrial applications, it is essential to ensure that the waste entering the conveyor belt is evenly distributed to prevent decrease of the positioning accuracy due to accumulation. In addition, results indicate that 17% of positioned bottles were misclassified as packages. The primary reason for this misclassification is that the wrapping on the surface of these bottles is identified as a package. Additionally, the partially obscured bottle loses its topography, leading the model to misclassify it as a package. Furthermore, in subsequent research, the volume of data in the MFIW dataset must be expanded to meet industrial application standards. This expansion will significantly enhance the accuracy in both positioning and classification. Another limitation is model deployment. Despite achieving a real-time FPS of over 30, the core framework of the model contains redundant calculations. This suggests that there is still potential for improvement in the computing speed of the model.

In future research, dual-angle or multi-angle vision-

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based sorting system will be explored. This approach aims to reduce waste misclassification caused by incomplete monitoring in single-angle vision systems. Simultaneously, the use of visual segmentation technology for waste identification will be explored. Combining these methods is expected to improve the model's detection performance for mixed foodinorganic waste.

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### DISINFECTION EFFICACY OF SLIGHTLY ACIDIC ELECTROLYZED WATER ON MICROORGANISMS: APPLICATION IN CONTAMINATED WASTE SORTING ROOMS ACROSS VARIED SCENARIOS

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#### Abstract

Various pathogenic microorganisms present in municipal solid waste (MSW) can pose significant hazards to both the environment and public health. Spraying Slightly Acidic Electrolyzed Water (SAEW) is effective method for decontaminating an microorganisms in the air and on surfaces in the waste sorting rooms. SAEW treatment, with an effective chlorine concentration (ECC) of 28.4-44.5 mg/L and a pH range of 5.0-6.5, was conducted in the waste sorting rooms of the old, high-rise, and villa residential communities in Shanghai, China. The efficacy of SAEW treatment was assessed by examining the microbial population in the air, on waste containers, on sanitation workers' hands, and the microbial community structure of MSW samples. SAEW treatment resulted in the total bacterial reduction ranging from 0.07 to 1.70 log<sub>10</sub> colony-forming units (CFU)/cm<sup>2</sup> on waste containers, with corresponding reduction efficiencies between 15.7% and 98.0%. Additionally, the positive rates of coliforms were decreased by 18.7%-95.2%. Furthermore, the application of SAEW demonstrated a significant impact on reducing airborne bacterial and fungal levels. SAEW was proven effective on object surfaces, in the air and on human skin, achieving disinfection efficiencies ranging from 22.7% to 54.3% on sanitation workers' hands. And the most significant inhibition of microbial growth was observed in the waste sorting room of the villa residential community. The microbial diversity and structure of MSW samples exhibited noticeable differences before and after the SAEW application. These findings suggest that SAEW holds significant potential as an ideal, environmentally friendly broad-spectrum disinfectant for preventing and controlling microbial contamination in the waste sorting rooms.

#### 1. Introduction

The abundant proliferation of diverse microorganisms within municipal solid waste (MSW) is attributed to the richness of organic matter and the complexity of substrates (Wang et al., 2017). Consequently, MSW is recognized as a significant "microbial pool", given its conductive conditions for the proliferation of microorganisms (Song et al., 2015). Several studies have indicated that MSW has the potential to host a variety of pathogenic microorganisms, including P. putida, E. casseliflavus, K. pneumoniae, C. lusitaniae and other pathogens (Liu et al., 2023; Madhwal et al., 2020; Piceno et al., 2017). These pathogens may pose infectious, allergenic, and toxic hazards, carrying inherent risks of contaminating the nearby surroundings, and thereby posing a significant threat to public health (Lavoie and Guertin, 2011). Waste collectors, in particular, have been demonstrated to suffer from a range of health impacts, encompassing rhinitis, asthma and conjunctivitis (Ayoola Nike et al., 2021; Collins and Kennedy, 2008; Lavoie and Guertin, 2011; Wouters et al., 2002). Currently, researches on microorganisms in MSW have primarily concentrated on landfills and transfer stations (Anand et al., 2022; Kalwasińska and Burkowska, 2013; Wang et al., 2021; Zhao et al., 2021b). However, there is a notable gap in the literature concerning the waste sorting rooms of residential communities, which represent the primary nexus for MSW collection. And the waste sorting rooms are the primary facilities that residents contact with throughout the entire process of MSW disposal, potentially resulting in detrimental health effects for nearby individuals, which is another reason why the waste sorting rooms deserves attention.

Numerous sanitization methods have been applied in waste sorting rooms to minimize microbial contamination, encompassing chlorine compounds, peroxide mixtures, ozone disinfection, and ultraviolet disinfection. Nevertheless, the constraints of enclosed spaces and unmanned indoor environments limit the use of ozone and ultraviolet disinfection in waste sorting rooms. Common chlorine disinfectants comprise sodium hypochlorite and chlorine dioxide, which have the disadvantages of corrosiveness, bleachability, volatility and skin irritation (Chelliah et al., 2023; Zang et al., 2019). Therefore, these constraints limit the widespread use of these sanitization methods. Due to its less negative effects on the environment and human health, Slightly Acidic Electrolyzed Water (SAEW) holds promise as an alternative decontamination technique.

SAEW with a pH range of 5.0-6.5 is produced through electrolysis of diluted HCl or NaCl in a membrane-free chamber (Yan et al., 2023; Zhu et al., 2023). The primary active chlorine compound in SAEW is typically the hypochlorous acid (HOCl) (Du et al., 2023;

Li et al., 2023). So far, SAEW has been found to exhibit potent microbicidal activity against a wide range of microorganisms, including Bacillus cereus, Bacillus subtilis, Listeria monocytogenes, Staphylococcus aureus. Salmonella spp, Salmonella enteritidis, Escherichia coli, and yeasts (Hao et al., 2010; Issa-Zacharia et al., 2010; Ni et al., 2015; Rahman et al., 2011). The microbicidal effects of SAEW are influenced by oxidation-reduction potential (ORP), effective chlorine concentration (ECC), and pH (Rahman et al., 2016; Sun et al., 2022; Zhao et al., 2021a). The high ORP characteristics of SAEW change the electron flow within microbial cells, leading to the disruption of cell membranes and subsequent microbial death. The effective chlorine efficiently destroys cell membranes and interacts with their DNA and mitochondria, ultimately resulting in the demise of the microorganisms. Due cost-effectiveness, to environmental friendliness, and broad-spectrum microbial properties, SAEW has been highlighted as an effective disinfection method in different application fields, without causing equipment corrosion, skin irritation, or safety concerns related to Cl<sub>2</sub> off-gassing (Li et al., 2016).

The sanitizing ability of SAEW to inactivate microorganisms on fruits, vegetables, animal houses, and hospitals have been extensively researched and validated (Du et al., 2023; Guan et al., 2023; Kong et al., 2023). Ding et al. (2015) revealed that the reductions of total aerobic bacteria, yeasts and molds on strawberries were 1.07 and 1.04 log<sub>10</sub> colony-forming units (CFU)/g after SAEW (ECC=34 mg/L and pH=6.49) treatment, respectively. Furthermore, spraying SAEW has been implemented to reduce microbial contaminant levels in animal facilities, particularly for surface and air disinfection purposes (Chuang et al., 2013; Zheng et al., 2016). Hao et al. (2013b) observed that SAEW (ECC=250 mg/L and pH=6.19) treatment curtailed the population of microorganisms on facility surface by 94.4% compared to controls. And Hao et al. (2013a) indicated that SAEW (ECC=250 mg/L and pH = 5.29-6.30) treatment resulted in airborne bacteria and fungi population reduction of 4.85 and 3.45 log<sub>10</sub> CFU/g, respectively. However, few studies have reported the effectiveness of SAEW on microorganisms in waste sorting rooms.

This study aims to evaluate the impacts of SAEW treatment on microorganisms' exposure levels among the waste sorting rooms of three distinct residential areas: old, high-rise, and villa residential communities in Shanghai, China. The microbial population of airborne, waste containers, and sanitation workers' hands were considered. The Illumina MiSeq high-throughput sequencing was used to examine the influence of spraying SAEW on the microbial community structure and the distribution of dominant bacteria and fungi within MSW during both summer and winter seasons. Additionally, pathogenic bacteria and fungi within MSW were identified. The results of this study will provide SAEW as a viable disinfection technique for controlling microbial contamination in the waste sorting rooms.

#### 2. Materials and methods

#### 2.1 Study area

The study was conducted in the waste sorting rooms of the old, high-rise, and villa residential communities in Shanghai, China (Fig. 1). The old residential community has the characteristics of poor infrastructure, high population density and large waste generation. The features of the high-rise residential community encompass relatively good infrastructure, moderate population density, and relatively larger waste generation. Nevertheless, the villa residential community is distinguished by good infrastructure, low population density, and low waste generation. The waste sorting room in the high-rise residential community employs a four-category waste classification system, including wet waste, residual waste, hazardous waste, and recyclable waste. In contrast, the waste sorting facilities in the old and villa residential communities follow a two-category method, sorting waste into residual and wet categories.



Fig. 1 The waste sorting rooms of (a) the old residential community; (b) the high-rise residential community; (c) the villa residential community

#### 2.1 Study design

The SAEW (ECC=28.4-44.5 mg/L and pH=5.0-6.5) was prepared using 9% HCl solution by a continuous SAEW generator. The generator was configured to operate at a voltage and current of 24 V and 2.5 A,

respectively. The SAEW generator consisted of an electrolytic cell without a membrane between the anode and cathode. And the materials of anode and cathode electrodes were platinum. The length, width and height of the generator were 550 mm, 550 mm, and 1260 mm, respectively. The waste sorting rooms were equipped with a spraying system comprising a high-pressure nozzle sprayer and several 150 mm diameter nozzles for spraying SAEW. SAEW was administered every half an hour, with each administration lasting for one minute. **Fig. 2** illustrates the schematic representation of SAEW. The generation process of SAEW can be explained as follows:

| Anode reaction: $2Cl^{-} \rightarrow Cl_2(\uparrow) + 2e^{-}$ | (1) |
|---|-----|
| $Cl_2+H_2O \rightarrow HOCl+H^++Cl^-$                         | (2) |

(3)

Cathode reaction:  $2H^++2e^-\rightarrow H_2(\uparrow)$ 



Fig. 2 Schematic representation of SAEW

Fig. 3a shows the study design for the efficiencies of SAEW for reducing microbial contamination in the waste sorting rooms. Microbial samples were collected from airborne, waste containers, and sanitation workers' hands. Sampling occurred over six non-consecutive days within the waste sorting rooms of three distinct residential areas: old, high-rise, and villa residential communities, all during the summer season. Specifically, sampling was scheduled at 9:00 A.M., 12:00 P.M., 5:00 P.M., 7:00 P.M., and 9:00 P.M. on Day 1, 2, 3, 5, 7, and 15, spanning from July 27, 2020, to August 10, 2020. Following the sampling at 9:00 P.M. on Day 2, SAEW was regularly sprayed for the subsequent 13 days. As shown in Fig. 3b, samples for microbial community were collected from residual waste and leachate of wet waste. The sampling process took place over two discontinuous days in the waste sorting room of the high-rise residential community during both summer and winter seasons. Specifically, sampling was conducted at 7:00 P.M. on Day 1 and Day 5, from August 18, 2021, to August 23, 2021 in summer, and from December 4, 2020, to December 9, 2020 in winter. Following the sampling at 7:00 P.M. on Day 1, spraying SAEW was conducted for the subsequent 5 days.



Fig. 3 Study designs for the application of SAEW for inactivating microbes in the waste sorting rooms (a) SAEW treatment on microorganisms; (b) SAEW treatment on microbial community

#### 2.1 Sampling and analysis

Microbial population analysis: The microbial samplers were used to simultaneously collect airborne bacteria and fungi. The average flow rate of the samplers was 28.3 L/min. The sampling duration was 5 min. For the waste containers and sanitation workers' hands, microbial samples from the control and treated groups were collected using sterile saline and phosphate-buffered saline (PBS), respectively. The object surfaces and human skin were swabbed at least 5 times using sterile swabs soaked in sterile saline or PBS. After the completion of sampling, the microbial samples were promptly transported to the laboratory. The airborne bacteria on nutrient agar plates and the airborne fungi on Sabouraud's agar plates were incubated at 37°C for 2 days and at 26°C for 5 days, respectively. The data from samples of airborne microorganisms is presented as time-weighted average (TWA) exposures in  $\log_{10}$  CFU/m<sup>3</sup>. The swab suspensions were diluted with sterile saline or PBS by the serial dilution method. 1.0 mL of serial dilutions were inoculated onto plate count agar to enumerate total bacterial count (48 h at 37°C) (Fraczek et al., 2014). After incubation, visible colonies were counted and presented as CFU/cm<sup>2</sup>. Coliforms presence was

Microbial community analysis: 500 mL of leachate was collected from the bottom of wet waste containers, mixed in a sterile beaker (1 L), and packed into three centrifuge tubes (50 mL) for 3 min of centrifugation. 50 g of residual waste was collected from residual waste containers, mixed in a sterile beaker (1 L), extracted by

verified through the multi-tube fermentation method.

PBS with a pH ranging from 7.2 to 7.4, and prepared by ultrasonic vibration at 160 W for 30 min. The residual waste was filtered by a screen, and the remaining liquid was also centrifuged for 3 min. After centrifugation, the supernatant in the centrifugal tubes was removed and more than 2 g of sediment was saved at 4°C for 24 h before DNA extraction.

The DNA was extracted by the FastDNA® Spin Kit for Soil (MP Biomedicals). To characterize bacterial community compositions, the V3-V4 region of the bacterial 16S rRNA genes from each sample was amplified using specific primers (338F and 806R). To explore the fungal community structure, the ITS1 region of the fungal 18S rRNA and 5.8S rRNA genes from each sample was amplified using specific primers (ITS1F and ITS2R). The extracted DNA were sequenced by the Illumina MiSeq platform (PE300, CA, USA).

#### 3. Results and discussion

#### 3.1 Effects of SAEW treatment on microorganisms

The disinfection efficacy of SAEW on waste containers and sanitation workers' hands is illustrated in Fig. 4. Compared with the control without SAEW treatment, the average populations of bacteria on waste containers were reduced by 0.07 to 1.70  $\log_{10}$  CFU/cm<sup>2</sup>, and the bacterial reduction efficiencies were 15.7%-98.0%. Notably, among the 21 microbial samples of waste containers in the waste sorting room of the villa residential community, 16 microbial samples had a total bacterial count of  $\leq$  1 CFU/cm<sup>2</sup>, which was a significant reduction. In the waste sorting rooms of the high-rise and old residential communities, the average populations of bacteria on wet waste containers consistently exceeded those of residual waste containers before and after the application of SAEW. This disparity could be attributed to perishable biomass with high organic matter and moisture in wet waste containers, which was conducive for the growth of microorganisms. And the surfaces and handles of wet waste containers commonly harbored substantial amounts of organic matter. This adherence further contributed to the conducive environment for microbial proliferation. And the bacterial reduction efficiencies of residual waste containers surpassed those of wet waste containers in the waste sorting room of the high-rise residential community. These findings may correlate with the presence of organic matter on the object surfaces, which reduces the bactericidal activity of SAEW (Rahman et al., 2016). Moreover, SAEW treatment resulted in bacterial reduction efficiencies on sanitation workers' hands of 22.7%-54.3%. These findings underscored the remarkable bactericidal effects of SAEW not only on object surfaces but also on human skin.





The effects of SAEW treatment on airborne were also examined (**Fig. 5**). The SAEW treatment resulted in the airborne microbial reduction of 0.19 to 0.52  $\log_{10}$ CFU/m<sup>3</sup> in the waste sorting rooms of the high-rise and villa residential communities, with corresponding reduction efficiencies of 34.7%-69.9%. This decline can be ascribed to the microbicidal properties of SAEW, as well as the simultaneous reduction in airborne dust levels (Zheng et al., 2014). However, the average populations of airborne bacteria did not show the same reduction trend with SAEW treatment in the waste sorting room of the old residential community. The results were primarily influenced by the presence of microbial pollution in the air of the toilet adjacent to the waste sorting room.





community; O-RC: old residential community; V-RC: villa residential community)

The results showed SAEW could effectively control microbial pollution in waste sorting rooms. It is well known that the antimicrobial activity of SAEW is dominated by HOCl. The antimicrobial action of HOCl is attributed to its penetration into microbial cells across through cell walls and cell membranes. HOCl can

attack the microbial cells from the outside and from within the cells. The antimicrobial activity of HOCl is believed to arise from the inhibition of enzyme activity essential for microbial growth, damage to membrane and DNA, potential impairment of membrane transport capacity (Li et al., 2016).

## 3.2 Effects of SAEW treatment on coliforms presence

Coliforms is commonly found in MSW, serving as indicators of contamination. The results of coliforms detection from the waste sorting rooms are illustrated in Fig. 6. The positive rates of coliforms on waste containers ranged from 72.7% to 100% before SAEW treatment, ranged from 4.3% to 81.3% after SAEW treatment, which showed a decrease of 18.7%-95.2%. Compared with the waste sorting rooms of the high-rise and old residential communities, the waste sorting room of the villa residential community showed the greatest decline in positive rates of coliforms. The main reason for this disparity might be the comprehensive ventilation measures cooperated with SAEW in the waste sorting room of the villa residential community. The number of indoor microorganisms can be effectively reduced by diluting indoor air with outdoor air. Before the application of SAEW, 57.1%-75% of the sanitation workers' hands tested positive for coliforms, while after SAEW treatment, the positive rate decreased to 0%-42.9%. The results demonstrated the presence of coliforms on waste containers and human skin, with SAEW significantly reducing the positive rates of coliforms.



**Fig. 6** Effects of SAEW treatment on coliforms presence in the waste sorting rooms of (a) the high-rise residential community; (b) the old residential community; (c) the villa residential community (RW: residual waste container; WW: wet waste container)

## **3.3 Effects of SAEW treatment on microbial community**

Bacterial community: As illustrated in Fig. 7a, the

bacterial community structure was investigated with MSW samples before and after SAEW treatment. The dominant phyla detected were Firmicutes and *Proteobacteria*, with a total abundance of 43.5%-99.3%. These findings align with previous researches conducted in landfills and waste containers of residential areas (Liu et al., 2023; Zhao et al., 2021b). After SAEW treatment, the relative abundances of Firmicutes were reduced by 12.9%-22.5%, whereas the relative abundances of Proteobacteria were increased by 3.6%-34.2%. Results indicated that SAEW had a significant impact on the relative abundances of dominant phyla. Shi et al. (2013) found that chlorine disinfection had a notable effect on the microbial structure, and water chlorination enhanced the relative abundances of Proteobacteria. Hypochlorous acid, the primary active component of SAEW, may be the cause for the increase in the relative abundances of Proteobacteria. The sterilization mechanism depended on the oxidative capacity of SAEW, which destroyed the cell wall of Firmicutes, resulting in the decrease in the relative abundances of Firmicutes.

As given in Fig. 7b, Lactobacillus and Acinetobacter were the dominant genera for all MSW samples, with a total abundance of 15.0%-93.0%. At the genus level, TM7a, Macrococcus, and Vagococcus were exclusively found in residual waste samples. The relative abundances of Lactobacillus reached 19.1%-91.8% in wet waste samples, obviously higher than those in residual waste samples (0.3%-13.8%). Meanwhile, the relative abundances of Lactobacillus showed a decrease of 10.5%-44.3% after SAEW treatment. Several studies have reported that pathogenic microorganisms, raising public health concerns, were detected in MSW across various MSW facilities (Song et al., 2023). Our study also revealed the presence of potential pathogens in MSW, although the relative abundances were not highest dominant. Acinetobacter is recognized as an opportunistic pathogen that is known to easily survive in humid environments and cause diseases such as pneumonia and meningitis. The relative abundances of Acinetobacter in residual waste samples were higher than those in wet waste samples. The relative abundances of Pseudomonas (0.4%-26.1%) were found to be the third highest, which were detected in all MSW samples. Pseudomonas is a common opportunistic pathogen with strong ability to degrade organic matter. Compared with summer samples, there were more Pseudomonas in winter samples, accounting for 2.8%-26.1% of the total abundances. Other pathogens such as Streptococcus and Enterobacter were also detected in MSW samples, suggesting that the presence of potential pathogenic species within MSW could pose notable microbial risks. Hence, it is crucial to consider microbial employing SAEW for controlling contamination within the waste sorting rooms.



Fig. 7 Relative abundances of bacterial community in MSW samples at (a) phylum level; (b) genus level

Fungal community: As shown in Fig. 8a, the distributions of the dominant fungi at the phylum level were mainly in *Ascomycota* and *Basidiomycota*, accounted for 97.5%-99.9% of total sequences. After SAEW treatment, the relative abundances of *Ascomycota* were decreased by 1.8%-22.7%, while the relative abundances of *Basidiomycota* were increased by 1.8%-21.5%, indicating that SAEW were beneficial for *Basidiomycota* growth, but not for *Ascomycota* growth. *Basidiomycota* displayed higher tolerance to disinfection and exhibited a competitive advantage over other fungal microorganisms, leading to an increase in relative abundances after SAEW treatment.

In terms of fungal taxonomy, a total of 25 fungal genera were identified (Fig. 8b). Among the fungal species detected, the dominant fungi at the genus level of residual and wet waste samples were different. The dominant fungal genus of wet waste samples was Kazachstania, and of residual waste samples was unclassified Dipodascaceae. After treatment with SAEW, the relative abundances of Kazachstania in wet waste samples and unclassified Dipodascaceae in residual waste samples were decreased by 11.7%-32.6% 14.3%-80.8%, and respectively, indicating that Kazachstania and unclassified Dipodascaceae were sensitive to SAEW.



**Fig. 8** Relative abundances of fungal community in MSW samples at (a) phylum level; (b) genus level

#### 4. Conclusions

The effects of SAEW treatment on microorganisms and microbial community in the waste sorting rooms of three distinct residential areas were proven in this study. The results demonstrated that SAEW (ECC=28.4-44.5 mg/L and pH=5.0-6.5) treatment effectively reduced the total bacterial counts on waste containers by 0.07 to 1.70 log10 CFU/m<sup>3</sup>, with corresponding reduction efficiencies of 15.7%-98.0%. And SAEW treatment resulted in bacterial reduction efficiencies on sanitation workers' hands of 22.7%-54.3%. In addition, SAEW effectively reduced the positive rates of coliforms on waste containers and sanitation workers' hands by 14.2%-95.2%. After SAEW treatment, the average airborne bacterial and fungal concentrations in the waste sorting rooms of the high-rise and villa residential communities were reduced by 0.19 to 0.52 log<sub>10</sub> CFU/m<sup>3</sup>, and the reduction efficiencies were 34.7%-69.9%. And the most significant microbial inhibition was observed in the waste sorting room of the villa residential community. Firmicutes and Proteobacteria were the top two dominant bacterial phyla, with a total abundance of 43.5%-99.3%. Lactobacillus and Acinetobacter were the dominant bacterial genera, with a total abundance of 15.0%-93.0%. Ascomycota and Basidiomycota were the top two dominant fungal phyla, accounted for 97.5%-99.9% of relative abundances. Kazachstania and unclassified Dipodascaceae were the top two dominant fungal genera, accounted for 0.25%-81.92%. After SAEW treatment, the relative abundances of Firmicutes and Ascomycota were decreased by 12.9%-22.5% and 1.84%-22.7%, respectively, while the relative abundances of *Proteobacteria* and *Basidiomycota* were increased by 3.55%-34.23% and 0.2%-21.5%, respectively, indicating that SAEW treatment caused variations in the microbial diversity and structure of MSW samples. Therefore, SAEW has shown promising efficiencies as an innovative disinfectant for preventing and controlling microbial contamination in the waste sorting rooms.

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## LACTIC ACID-BASE CARBON SOURCE ORIENTED DERIVED FROM FOOD WASTE: BIOCONVERSION OPTIMIZATION AND DENITRIFICATION EVALUATION

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#### ABSTRACT

The lactic acid fermentation supernatant of food waste (FSFW-LA) is an excellent carbon source for denitrification regarding performance and cost. Currently, limited attention has been paid to the concentration of lactic acid and its composition in the final product. In this study, five types of liquid carbon sources were obtained under optimal conditions to ensure a high concentration and percentage of the target products. Among them, FSFW-LA reached 68.1 g/L (81.8%, w/w) of lactic acid by oriented bioconversion and possessed denitrification parameters closest to sodium acetate. Under the combined long-term operation of the SBR system with domestic wastewater, the TN and COD removal in the effluent after the addition of FSFW-LA stabilized at 96% and 84%, respectively, similar to sodium acetate (96% and 85%). Overall, the denitrification capabilities of high-quality FSFW-LA were explored, providing details on economic carbon source production.

**Keyword:** Perishable garbage; Anaerobic fermentation; *Enterococcus mundtii*; Nitrate removal; Sequencing batch reactor

#### INTRODUCTION

Human activities have dramatically altered the global nitrogen cycle by importing excess nitrogen into terrestrial ecosystems, resulting in nitrogen pollution that affects both ecosystem and human health (Fowler et al., 2013). However, the carbon-to-nitrogen ratio (C/N) of domestic wastewater tends to be low in China, which inhibits nitrogen removal effect (Sun et al., 2010). Traditional commercial carbon sources such as glucose, methanol, and sodium acetate (NaAc), have been disappointing in terms of sludge yield, safety, and acquisition costs (Dhamole et al., 2015). In China, If NaAc (30%, 1000  $\frac{1}{2}$ ) is used to adjust to the ideal C/N=7 range, an additional 0.98 ¥ per ton of wastewater needs to be borne, which undoubtedly puts a great pressure on municipal wastewater treatment plants (WWTPs) (Fu et al., 2023; Zeng et al., 2024). Food waste (FW) is useful for the preparation of denitrification carbon sources (Yan et al., 2018), with low cost, high organic content, and fermentability as its natural advantages.

In this study, the anaerobic bioconversion process of FW was optimized to obtain the highest possible quality of carbon sources under suitable conditions and to compare these carbon sources with NaAc for denitrification performance, thus attempting to further improve the resourcefulness of FW and alleviate the pressure of the current application of external carbon sources in WWTPs.

#### MATERIALS AND METHODS Experimental materials

Fresh FW was obtained from the cafeteria of the University of Science and Technology Beijing, China. After manual decontamination, then made into a homogeneous slurry by milling with a macerating grinder. Two types of inocula were used for oriented bioconversion: mesophilic anaerobically digested sludge obtained from the Gaoantun Sludge Treatment Center in Beijing, China, and Enterococcus mundtii CGMCC 22227, which was kept in the laboratory. The *E. mundtii* was stored at -80 °C in tubes containing 15 % (v/v) glycerol, and cells were prepared for growth and inoculation using de Man, Rogosa, and Sharpe (MRS) medium, the composition of the MRS medium and preparations before inoculation were consistent with a previous study. The activated sludge for denitrification was obtained from the Qinghe Wastewater Treatment Plant, Beijing, China. NaAc was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

#### <u>Preparation of different denitrification carbon</u> <u>sources by food waste</u>

Details of the production of the five liquid carbon sources are described in Fig. 1, as Raw food waste (FW-Raw), Saccharified food waste (FW-Sacc.), Spontaneous fermentation supernatant of food waste (FSFW-Spon.), LA fermentation supernatant of food waste (FSFW-LA) and VFAs fermentation supernatant



Fig. 1. Detailed preparation process for five kinds of denitrification carbon sources produced from food waste.

#### **Denitrification potential test**

Activated sludge was washed three times with NO3-N-free domestic wastewater to remove residual nitrogenous compounds and organic matter. A total of 2.5 L of NO3<sup>-</sup>-N-free domestic wastewater was diluted with adjusted MLSS to 2500  $\pm$  500 mg/L and transferred to five conical flasks, each with a working volume of 500 mL. The mixture was flushed with nitrogen to ensure an anaerobic environment. Subsequently, KNO3 was added to obtain a final NO<sub>3</sub><sup>-</sup>N concentration of 30 mg/L, and carbon sources (FW-Raw, FW-Sacc., FSFW-Spon., FSFW-LA and FSFW-VFAs) were added separately to make SCOD=300 mg/L (C/N=10). The mixture was withdrawn from each conical flask at regular intervals, and analyzed for NO3--N, NO2--N, and SCOD after passing through a 0.45 µm membrane.

#### SBR system

Long-term stability of carbon sources explored in the SBR system with domestic wastewater. The reactor, with an effective working volume of 4 L, was equipped with an aeration pump and stirrer. The operating procedure of the SBR system was as follows: anaerobic mixing for 2 h, aerobic aeration for 4 h, anoxic mixing for 4 h, and precipitation for 2 h, with 12 h as a cycle, the system was operated for 30 consecutive cycles. The reactor was inoculated with activated sludge (MLSS=2500±500 mg/L), and the C/N was adjusted to 6.5. Water samples were periodically removed to monitor the changes in NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N, and COD.

#### <u>Analytical</u>

The measurements of TCOD and SCOD were made with reference to the standard, "*HJ/T399-2007*". The concentrations of LA and VFAs were measured by High Performance Liquid Chromatography (LA-20A; Shimadzu, Kyoto, Japan). TN "*HJ636-2012*", NH<sub>4</sub>+-N "*HJ535-2009*", NO<sub>3</sub><sup>-</sup>-N "*HJ/T346-2007*", NO<sub>2</sub><sup>-</sup>-N "*GB7493-1987*". MLSS and MLVSS were measured by applying a gravimetric method. The phenol sulfate method was used for carbohydrate measurements.

#### **RESULT AND DISCUSSION**

#### <u>Carbon sources produced from food waste</u> <u>Fermentation performance and composition</u> <u>analysis</u>

All five carbon sources were derived from FW. Among them, FW-Raw and FW-Sacc. were relatively simple to obtain, whereas FSFW-LA, FSFW-VFAs, and FSFW-Spon. must be obtained through anaerobic fermentation. Different inocula and fermentation times significantly affected the final product concentration and composition (Fig. 2).

The concentration of LA in FSFW-LA group rapidly increased to 67.9 g/L within 48 h (Fig. 2a), and there are some slight fluctuations during 48 h to 120 h. At 120 h, LA accounted for 81.8% (w/w) of the products containing ethanol, LA, and VFAs, dominating the entire fermentation process. However, prolonged fermentation time could lead to a decrease in the concentration and proportion of LA, from 68.1 g/L and 81.8% (120 h) to 63.5 g/L and 71.9% (168 h), respectively. In contrast, the product changes in FSFW-VFAs group inoculated with digested sludge (Fig. 2b) were quite different from those of FSFW-LA. The VFA concentration reached 11.9 g/L after anaerobic fermentation for 36 h. As the fermentation progressed to 168 h, VFAs (32.6 g/L), composed of propionate (46.9%), butyrate (36.3%), valerate (10.3%), and acetate (6.5%), became the major component, accounting for 83.1% (w/w) of the products containing ethanol, LA, and VFAs, while LA was only 2.9 g/L. This result indicates that a sufficient fermentation time (168 h) was needed for the FSFW-VFAs group to ensure a suitable product composition. The presence of propionate and butyrate has been shown to reduce the by-products (N<sub>2</sub>O and NO) of denitrification (Zhu & Chen, 2011), suggesting that FSFW-VFAs has the potential to be used as a carbon source for denitrification. Compared with FSFW-LA and FSFW-Spon., the total concentration of acid products (LA and VFAs) in FSFW-VFAs decreased significantly

from 66.2 g/L (120 h) to 35.5 g/L (168 h). The microorganisms in the digested sludge metabolized the

organic acids (LA and VFAs) produced for biogas generation (Liu et al., 2020), especially at the later stag



**Fig. 2.** The changes in product composition of different anaerobic fermentation with food waste as substrate in open mode. (a) FSFW-LA, *Enterococcus mundtii* inoculation, 43 °C, pH control at 6.8; (b) FSFW-VFAs, anaerobic digestion sludge inoculation, 37 °C, pH control at 6.0; (c) FSFW-Spon., non-inoculation, 37 °C, without pH control.

| Table 1 Property of five kinds of carbon sources derived from food waste |               |                |               |               |               |
|--|---------------|----------------|---------------|---------------|---------------|
| Parameter  | FW-Raw        | FW-Sacc.       | FSFW-LA       | FSFW-VFAs     | FSFW-Spon.    |
| pН   | 5.2±0.1       | 5.1±0.1        | 7.6±0.2       | 5.0±0.1       | 3.2±0.1       |
| TCOD (g/L)   | 84.3±3.7      | 88.5±2.3       | 86.7±4.9      | 64.1±4.5      | 76.5±2.4      |
| SCOD (g/L)   | 75.7±1.7      | $80.5 \pm 1.8$ | 73.7±3.0      | 49.5±2.9      | 63.4±2.2      |
| Total protein (g/L)  | $0.3{\pm}0.3$ | $0.5\pm0.2$    | $0.4{\pm}0.2$ | $0.1{\pm}0.1$ | $0.3{\pm}0.1$ |
| Total carbohydrate (g/L)   | 66.3±2.0      | 72.2±2.1       | 5.7±0.1       | 2.1±0.1       | 30.3±1.1      |
| VFAs (g/L)   | 5.2±0.1       | $5.0\pm0.1$    | 11.1±0.4      | 32.6±1.2      | $3.4{\pm}0.2$ |
| Lactic acid (g/L)  | 8.7±0.1       | $1.9{\pm}0.1$  | 68.1±3.7      | 2.9±0.1       | 22.0±0.6      |
| NH4 <sup>+</sup> -N (g/L)  | $0.7{\pm}0.1$ | $1.1\pm0.1$    | $0.2{\pm}0.1$ | $0.2{\pm}0.1$ | $0.2{\pm}0.1$ |
| TN (g/L)   | $1.2\pm0.1$   | $1.4{\pm}0.1$  | $0.8 \pm 0.3$ | $1.1{\pm}0.1$ | $1.2{\pm}0.1$ |
| TP (g/L)   | $0.2{\pm}0.1$ | $0.2{\pm}0.1$  | $0.2{\pm}0.1$ | $0.1{\pm}0.1$ | 0.2±0.1       |

Note: The values were the mean  $\pm$  standard deviation (n = 3).

of fermentation in the FSFW-VFAs group. In addition, as shown in Fig. 2c, the LA concentration in FSFW-Spon. group gradually increased and stabilized at 22 g/L (120 h) without exogenous microorganism inoculation and pH control, which was quite higher than that of the VFAs (3.4 g/L) and ethanol (3.6 g/L) in fermentation liquid. A comparison of Fig. 2a and 2c shows that inoculation with *E. mundtii* and pH control substantially increased the concentration of LA (from 22 g/L to 68.1 g/L), resulting in oriented and efficient bioconversion.

The composition of the products in the fermentation broth was affected by fermentation time, suggesting that the microbial community may have also changed. Considering the concentration, percentage, and stability of the target product in each group, the fermentation supernatant at 120, 168, and 120 h was selected as the carbon source for FSFW-LA, FSFW-VFAs, and FSFW-Spon, respectively, for subsequent analysis of the microbial community.

# Denitrification performance of different carbon sources derived from food waste

To compare the denitrification performance of the five carbon sources (FW-Raw, FW-Sacc., FSFW-Spon., FSFW-LA, and FSFW-VFAs) produced from FW with commercial NaAc carbon source (commonly used in China), the batch tests were carried out for 4 h at C/N=10, with a high C/N setting to ensure that the experiments could carry out smoothly. Table 4 lists the characteristics of the five carbon sources. Notably, FSFW-LA possessed the lowest NH<sub>4</sub><sup>+</sup>-N and TN content (0.2 g/L, 0.8 g/L), suggested that the application of FSFW-LA as a denitrification carbon source resulted in a slight nitrogen loading impact on the wastewater treatment system.

#### <u>Variations of NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and SOCD</u> <u>concentrations</u>

Changes in NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and SCOD were detected during the denitrification test with the addition of different carbon sources, as shown in Fig. 2. The water samples with NaAc, FSFW-LA, and FSFW-VFAs as carbon sources for denitrification exhibited complete degradation of NO<sub>3</sub><sup>-</sup>-N within 60, 90, and 120 min, respectively, whereas FSFW-Spon. addition group still had a residual NO<sub>3</sub><sup>-</sup>N concentration of 3.8 mg/L after 240 min (Fig. 2a). Denitrification occurred only slightly in FW-Raw and FW-Sacc. groups, with NO<sub>3</sub><sup>-</sup>N reduction rates of 8.4% and 11.6%, respectively, after 240 min. It indicated that small molecules, such as NaAc, LA, and VFAs are easily utilized by microorganisms in the denitrification process, which can completely consume NO<sub>x</sub><sup>-</sup>N and possess better denitrification effect.



Fig. 2. Denitrification performance with different external carbon sources derived from food waste in

batch test. (a)  $NO_3^-N$ ; (b)  $NO_2^-N$ ; (c) SCOD.

Regarding to NO<sub>2</sub><sup>--</sup>N variation, NO<sub>2</sub><sup>--</sup>N accumulation was observed in all the carbon source addition groups (Fig. 2b). For groups with NaAc, FSFW-LA, and FSFW-VFAs as carbon sources, the accumulated NO<sub>2</sub><sup>--</sup>N was fully reduced within 60, 90, and 150 min, respectively. Furthermore, NaAc resulted in the highest NO<sub>2</sub><sup>--</sup>N accumulation (21.6 mg/L), whereas FSFW-LA showed the lowest NO<sub>2</sub><sup>--</sup>N accumulation (11.5 mg/L). The residual NO<sub>2</sub><sup>--</sup>N concentration in the FSFW-Spon. was still 19.5 mg/L after 240 min of denitrification, indicating that the content of the high-quality carbon source (LA) was limited (30.8%) and the remaining macromolecular sugars (47.8%) were not sufficient to support further reduction of  $NO_2$ -N.

The degradation of SCOD also illustrates the utilization of external carbon sources during denitrification (Fig. 2c). With the addition of NaAc, FSFW-LA, and FSFW-VFAs as carbon sources, the SCOD was rapidly consumed in the first 60 min, and the SCOD concentration stabilized after 120 min of reaction, with utilization rates of 75.3%, 75.3%, and 75.9%, respectively. For FW-Raw, FW-Sacc. and FSFW-Spon. addition groups, the SCOD utilization rates were only 8.5%, 11.4%, and 40.0%, respectively, which were significantly lower than those in the previous three groups.

The above values were calculated using the corresponding parameters to compare the denitrification performance (Table 2). As the external carbon source for denitrification, NaAc has the highest V<sub>DN</sub> of 12.85 mgNO<sub>x</sub>-N/(gMLSS·h), followed by FSFW-LA with 9.98 mgNO<sub>x</sub>-N/(gMLSS h). Based on the perspective of P<sub>DN</sub>, FSFW-LA still possessed the closest value to commercial NaAc (0.14 mgNO3<sup>-</sup>-N/mgSCOD) at 0.13 mgNO<sub>3</sub><sup>-</sup>-N/mgSCOD, indicating that the FSFW-LA had the highest potential to serve as a promising carbon source for denitrification. In addition, the Y<sub>DN</sub> of NaAc was the lowest at 0.60 gSCOD/gSCOD, followed by FSFW-LA (0.63 gSCOD/gSCOD). The results showed that among the five types of liquid carbon sources prepared from FW, FSFW-LA had the best denitrification performance and was almost identical to commercial NaAc in all the parameters listed in Table 2. Considering the cost and high NO<sub>2</sub>-N accumulation problem caused by using NaAc in these test batch experiments, FSFW-LA is considered an excellent alternative for future applications in the biological removal of nitrogen.

| Carbon Source | μSCOD          | µNO3⁻-N         | $V_{DN}$                           | P <sub>DN</sub>                | Y <sub>DN</sub> |
|---------------|----------------|-----------------|------------------------------------|--------------------------------|-----------------|
|               | (%)            | (%)             | (mgNO <sub>x</sub> -N/(gMLSS · h)) | (mgNO3 <sup>-</sup> -N/mgSCOD) | (gSCOD/gSCOD)   |
| NaAc          | 75.3±4.9       | $100.0{\pm}0.1$ | 12.85±0.87                         | $0.14{\pm}0.04$                | $0.60{\pm}0.19$ |
| FSFW-LA       | 75.3±4.0       | $100.0\pm0.1$   | $9.98{\pm}0.48$                    | $0.13 \pm 0.01$                | $0.63 \pm 0.17$ |
| FSFW-VFAs     | 75.9±2.5       | $100.0{\pm}0.1$ | $5.28 \pm 0.42$                    | $0.12 \pm 0.02$                | $0.66 \pm 0.16$ |
| FSFW-Spon.    | $40.0 \pm 3.8$ | $85.5 \pm 4.0$  | $1.01{\pm}0.01$                    | $0.11 \pm 0.02$                | 0.69±0.15       |
| FW-Raw        | $8.5 \pm 0.8$  | $8.4{\pm}0.9$   | $0.14{\pm}0.40$                    | $0.06 \pm 0.01$                | $0.84{\pm}0.08$ |
| FW-Sacc.      | $11.4\pm0.6$   | $11.6\pm0.9$    | $0.10{\pm}0.03$                    | $0.04{\pm}0.02$                | $0.90{\pm}0.05$ |

 Table 2
 Nitrogen removal performance with different external carbon sources

#### Long-term operation in SBR system

An SBR system was constructed in which FSFW-LA and NaAc were applied as a single carbon source supplement for enhanced domestic wastewater denitrification for a long-term under C/N=6.5 to explore the practical value of FSFW-LA. In this study,

the addition of carbon source after aeration was considered to avoid heavy consumption of the carbon source by nitrifying bacteria in the previous stage, which prevented subsequent denitrification from proceeding adequately.

Fig. 3a shows the changes in nitrogen content using

FSFW-LA as an external carbon source. The final effluent NH<sub>4</sub><sup>+</sup>-N concentration was still lower than 0.8 mg/L (removal rate >97%) in the absence of aerobic transformation at front end, indicating that the system has satisfactory NH<sub>4</sub><sup>+</sup>-N removal ability. The concentrations of NO3<sup>-</sup>-N and NO2<sup>-</sup>-N in the effluent were both lower than 0.5 mg/L during the operation period, which indicated that the denitrification efficiency was excellent because the activity of denitrifying bacteria was high and the accumulation of NO2-N was not observed. The TN concentration stabilized below 1 mg/L, and the removal rate reached a high level (>96%), which was essentially the same as when NaAc was added (Fig. 3b). According to the SBR system with NaAc as the carbon source, the NH4<sup>+</sup>-N

and TN removal exceeded 98% (<0.6 mg/L) and 96% (<1.0 mg/L), respectively. In addition, changes in COD were examined (Fig. 3c and 3d). FSFW-LA also achieved a COD removal of 84%, which is very close to the result obtained using NaAc as an external carbon source (85%).

These data demonstrate that FSFW-LA has the potential for long-term carbon source supplementation in SBR system. It can also be seen from the data and graphs that although NaAc is usually used as a carbon source in WWTPs, the microorganisms in the sludge (untamed) were able to utilize FSFW-LA easily and directly, which suggests that FSFW-LA is highly applicable and easily replicated in current WWTPs.



Fig. 3. The variations of nitrogen forms and COD with the addition of lactic acid fermentation supernatant of food waste and sodium acetate as carbon sources in SBR system during long-term operation. (a) nitrogen forms variation in SBR system with FSFW-LA; (b) nitrogen forms variation in SBR system with NaAc; (c) COD variation in SBR system with FSFW-LA; (d) COD variation in SBR system with NaAc.

To further investigate the complete single-cycle (12 h) nitrogen removal behavior within SBR system, samples were taken every 30 min,  $NH_4^+$ -N,  $NO_3^-$ -N,  $NO_2^-$ -N, and COD were measured after passing through a 0.45 µm membrane. The results showed that the denitrification behaviors of FSFW-LA and NaAc were almost identical. The concentration of  $NH_4^+$ -N in both groups rapidly decreased from 29.5 mg/L at 0 min to 19.5 mg/L at 30 min. As the reaction proceeded to 240 min,  $NH_4^+$ -N was completely degraded (<0.2 mg/L) in both reactors.  $NO_3^-$ -N was produced immediately after entering the aeration phase and gradually increased,

achieving a maximum mean value of 19.4 mg/L at 360 min, which was attributed to the insufficient carbon sources and the absence of simultaneous nitrification-denitrification process in this stage, which kept NO3--N accumulating without being converted to nitrogen. After entering the denitrification stage (360-600 min), due to the additions of carbon source (Fig. 4a for FSFW-LA, Fig. 4b for NaAc), the concentration of NO3-N in both FSFW-LA and NaAc decreased rapidly, and was completely degraded (nearly 0 mg/L) at 480 and 420 min, respectively. The shorter degradation time of NO3-N in NaAc may be attributed

to its relatively homogeneous composition compared with that of FSFW-LA, leading to simpler microbial metabolic pathways. Regarding NO<sub>2</sub><sup>-</sup>-N, NaAc had a maximum value of 6.4 mg/L at 390 min, far exceeding FSFW-LA (2.5 mg/L) at the same moment. The COD concentrations in effluents of two reactors were 16.9 mg/L (FSFW-LA) and 24.5 mg/L (NaAc), with removal rates of 91% and 86%.

The nitrification process was carried out completely in both groups, indicating the difference in type of carbon source had less influence on the nitrification process. However, the addition of carbon sources leads to a slowdown in the growth of autotrophic microorganisms, such as nitrifying bacteria, and use of NaAc leads to a decrease in the relative abundance of nitrification genes (Zhang et al., 2024). Therefore, FSFW-LA with a similar denitrification performance is a more satisfactory and attractive carbon source considering its lower application cost, nitrite accumulation, and nitrification gene inhibition.



Fig. 4. Single-cycle nitrogen forms and COD various in SBR system with the addition of lactic acid fermentation supernatant of food waste and sodium acetate as carbon source. (a) FSFW-LA addition; (b) NaAc addition.

#### CONCLUSIONS

Lactic acid was easily obtained from food waste by oriented bioconversion and reached 68.1 g/L (81.8%, w/w) under optimal condition in this study,

corresponding functional strains are enriched and dominated. Lactic acid fermentation supernatant possesses nearly identical denitrification parameters to those of sodium acetate, stabilizing TN and COD removal above 96% and 84%, respectively, in a long-term SBR system. This kind of carbon source also possessed lower cost and slighter NO<sub>2</sub><sup>-</sup>-N accumulation, proved that it had considerable superiority as an external carbon source to improve the denitrification capacity of wastewater treatment.

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## HIGHLY EFFICIENT LACTIC ACID PRODUCTION FROM KITCHEN WASTE IN OPEN FERMENTATION MODE WITH BIOLOGICAL CARBON FIXATION

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#### Abstract

The valorization of organic solid waste to lactic acid (LA) in open fermentation systems has attracted tremendous interest in recent years. In this study, a highly efficient oriented LA bioconversion system from food waste (FW) in open mode was established. The maximum LA production was 115 g/L, with a high yield of 0.97 g-LA/g-total sugar. FW is a low-cost feedstock for LA production, containing indigenous hydrolysis and LA-producing bacteria (LAB). Saccharification and real-time pH control were found to be essential for maintaining LAB dominantly in open systems. The oriented LA bioconversion exhibited the capacity for biological carbon fixation by reducing CO2 emissions by at least 21 kg per ton of FW under anaerobic conditions.

Keyword: Food waste; Open fermentation; Lactic acid; Biological carbon fixation; Biorefinery

#### **INTRODUCTION**

The current global average annual production of Food Waste (FW) is 1.3 billion tons, and is expected to increase to 2.2 billion tons by 2025 (Kaur et al., 2020). FW rich in nutrients represents one of the best substrate materials for biorefining. Fermentation production of LA is currently a common approach in the industry because it accounts for approximately 90 % of LA production (Wischral et al., 2019). Several studies have reported the ability of FW as feedstock to produce LA through fermentation (Buhlmann et al., 2020; Kim et al., 2016), while homotypic fermentation lactic acid bacteria (LAB) convert glucose almost completely to LA through the Embden-Meyerhof pathway (EMP). There is almost no loss of the carbon source during microbial metabolism, which means that there is nearly no CO<sub>2</sub> emission during the process. While autoclaving causes a Maillard reaction in the fermentation substrate medium, which results in sugar loss and increased production costs. An open fermentation system without sterilization has great advantages in biochemical production because it saves energy by omitting

autoclave operations.

In this study, we developed an efficient LA conversion process using indigenous LAB in FW and exogenous *Enterococcus mundtii* within an open fermentation system. The effects of glycosylase addition, inoculum conditions, and pH adjustment strategies on oriented LA bioconversion were also investigated. Furthermore, to gain insight into fermentation performance under different condition were analyzed. In addition, CO<sub>2</sub> emissions during highly efficient oriented LA bioconversion from FW were detected and evaluated in this study.

#### MATERIALS AND METHODS Materials

FW was obtained from a student canteen at the University of Science and Technology Beijing. *Enterococcus mundtii* was obtained from the Chinese General Microbial Strain Collection Management Center. The strain was stored at 80 °C in tubes containing 15 % (v/v) glycerol. The cells were prepared for growth and inoculation using de Man, Rogosa, and Sharpe (MRS) medium. The medium was adjusted to an initial pH of 6.8 and sterilized at 115 °C for 15 min. One milliliter of strain stock was transferred aseptically to 9-mL MRS medium (10 %, v/v) and incubated at 43 °C for 12 h. Then, preculture was produced by transferring 10 mL of the refreshed culture to 90-mL MRS medium and incubating it at 43 °C for 9 h.

#### LA fermentation method for FW

Before saccharification by glycosylase and LA fermentation, the FW was pretreated with water at a ratio of 1:0.5 (m/v) by boiling at 80 °C for 1.5 h to remove oil and grease. Glycosylase (2 g/kg FW mixture) was used for saccharification. The glycosylase used was amyloglucosidase from *Aspergillus niger*, which could turn all starch converted into glucose. Enzymatic hydrolysis was performed at 60 °C with stirring at 150 rpm for 6 h. The unsaccharified or saccharified FW mixture was crushed and sieved through a steel screen

 $(\Phi = 1 \text{ mm})$  as the fermentation substrate.

LA fermentations were carried out in 1-L fermenters with a working volume of 400 mL, containing either unsaccharified or saccharified FW substrate without sterilization by charging with nitrogen to maintain anaerobic conditions. Open LA fermentation with exogenous *E. mundtii* was performed at 43 °C with an inoculation ratio of 10 % (v/v). Two pH adjustment strategies were employed in this study. One strategy was real-time pH control, and the other involved only adjusting the initial pH.

To evaluate and compare the carbon loss (CO<sub>2</sub> emission) of different bioconversion processes from FW, 450 mL of saccharified FW substrate was added into an 800-mL bioreactor without autoclaving by inoculating 50 mL of *E. mundtii* preculture broth, sterilized water, and yeast seed broth. Starting fermentation as described above. Bioconversion without inoculation was performed at 37 °C without pH control. Ethanol production from FW using yeast was performed at 35 °C without pH control. The gas emissions in each group were recorded using a Milli-gas counter and detected daily by gas chromatography (GC).

#### Analytical methods

The broth samples were centrifuged for 20 min at 8,300  $\times$  g and 4 °C and the supernatant was passed through a 0.22 µm filter membrane. The concentrations of glucose, LA, acetic acid, and ethanol were analyzed chromatography high-performance liquid using equipped with a Shodex SH1011 column and a refractive index detection (RID). The column temperature was set at 60 °C and the mobile phase was 5 mM H<sub>2</sub>SO<sub>4</sub> at a flow rate of 1 mL/min. The injection volume was 10 µL. pH was determined using a pH meter PHS-3C. Total sugar concentration was determined by the phenol-sulfuric acid method, using glucose as a standard. The concentration of the reducing sugars was determined using the 3, 5-dinitrosalicylic acid (DNS) assay.

Evolved gases were measured and analyzed using GC packed with ShinCarbon ST Micropacked Column and thermal conductivity detector (TCD). Argon was used as the carrier gas. The column, detector, and injection port temperatures were set to 190 °C, 200 °C, and 190 °C, respectively.

#### **RESULT AND DISCUSSION**

#### Optimization of open efficient oriented LA bioconversion process from FW

To explore the performance of indigenous LAB in FW, the FW substrate was not sterilized, saccharified, added to 10 % (v/v) sterile water, and then subjected to open batch fermentation with continuous real-time pH control of 6.8 (Group B; Fig. 1B). The control group was subjected to the FW substrate without saccharification (Group A; Fig. 1A). Indigenous microorganisms in the system produced 50.6 g/L LA after 96 h of fermentation without the addition of glycosylase for FW saccharification. Because the FW was not sterilized before fermentation, resulting in acetic acid and ethanol as by-products of LA fermentation being generated, which reached 27.9 g/L and 50.3 g/L at 96 h in fermentation broth, respectively (Fig. 1A). Thus, the yield was only 0.42 g-LA/g-total sugar in the FW substrate without saccharification and exogenous inoculation. However, after saccharification of FW by adding glycosylase, the LA produced by indigenous microorganisms in the open FW fermentation system increased to 74.8 g/L after 36 h (Fig. 1B), corresponding to a LA yield of 0.63 g-LA/g-total sugar in FW substrate.

Saccharification treatment increased the initial concentration of glucose in the FW substrate, which facilitated utilization of the substrate by indigenous LAB and probably dominated the LAB in the open fermentation process, inhibiting the survival of indigenous acetic acid- and ethanol-producing bacteria. The bioconversion of FW to LA by exogenously inoculating the efficient LAB E. mundtii in open fermentation was investigated. To further improve the LA yield, after saccharification of the FW, open batch fermentation was carried out with the addition of 10 % (v/v) E. mundtii and continuous real-time pH control at 6.8 (Group D; Fig. 1D). Meanwhile, the control group without saccharification treatment of the FW substrate (Group C; Fig. 1C) was inoculated with E. mundtii. LA production was substantially enhanced by exogenous LAB addition in groups C and D compared to groups A and B, respectively. In group C without saccharification, LA reached a maximum concentration of 102 g/L after 120 h of fermentation (Fig. 1C), corresponding to 0.86 g-LA/g-total sugar yield, and the by-products acetic acid and ethanol reached maximum concentrations of 12.8 and 11.4 g/L at 96 and 48 h, respectively. To improve LA yield, saccharification was performed by adding glycosylase to the FW substrate before fermentation to improve the oriented LA Hydrolysis with bioconversion performance. glycosylase addition increased the initial glucose concentration in the open FW fermentation system (Group D) to 72.3 g/L, and the LA concentration was 115 g/L after 72 h of fermentation (Fig. 1D), corresponding to a 0.97 g-LA/g-total sugar yield, which improved the oriented conversion of LA from FW.

The by-products acetic acid and ethanol reached maximum concentrations of 8.03 and 7.35 g/L at 120 h and 96 h (Group D; Fig. 1D), respectively. In this study, highly efficient oriented bioconversion of FW to LA was established with high LA concentration (115 g/L), yield (0.97 g-LA/g-total sugar) and production rate (6.08 g/L/h) by exogenously inoculating *E. mundtii* in open system. *E. mundtii* is considered as an efficient LAB, which could suffer the culture conditions with

high sugar (160 g/L) and LA (150 g/L) concentrations without substrate and product inhibitions during LA fermentation. The above experiments showed that LA concentration and yield were in the following order: inoculated and saccharified group (Group D) > inoculated but not saccharified group (Group C) > non-inoculated but saccharified group (Group B) > non-inoculated and not saccharified group (Group A). The by-products (acetic acid and ethanol) of the two

inoculated groups (Groups C and D) were significantly lower than those of the non-inoculated group (Groups A and B). The maximum LA production rate (g/L/h) was as follows: inoculated and saccharified group (6.08; Group D) > non-inoculated but saccharified group (3.26; Group B) > inoculated but not saccharified group (2.45; Group C) > non-inoculated and non-saccharified group (0.93; Group A).



**Fig. 1. Effects of inoculation and saccharification of LA production from FW under pH regulation.** (A) Group A, without saccharification, non-inoculation, pH control at 6.8; (B) Group B, saccharification, non-inoculation, pH control at 6.8; (C) Group C, without saccharification, inoculation, pH control at 6.8; (D) Group D, saccharification, inoculation, pH control at 6.8.

Therefore, inoculation with exogenous *E. mundtii* significantly increased LA production and yield and inhibited the production of by-products by indigenous microorganisms in FW substrates. Meanwhile, a high initial fermentable sugar concentration could substantially increase the production rate of LA and shorten the fermentation time, thus contributing to a reduction in LA production costs.

The optimal pH for the growth of *E. mundtii* is 6.8, the LA bioconversion processes were compared using two different strategies of pH adjustment, that is, continuous real-time pH control at 6.8 or initial pH adjustment to 6.8, under the same incubation conditions; the results are shown in Figs. 1 and 2. As shown in Fig. 2, the initial control of pH 6.8 in the fermentation system did not exceed 12 g/L LA in all four groups

(with different inoculation and saccharification conditions; Groups E, F, G, H), and the growth and metabolism of LAB were severely inhibited. In contrast, the maximum LA concentration increased by 4.2-fold with continuous real-time regulation of pH 6.8. Continuous real-time pH control neutralized LA production in the system and had a buffering effect on the pH of the fermentation system. Real-time control of pH significantly increased the LA concentration in the fermentation system. Regarding the initial pH- adjusted groups (Groups E-H; Fig. 2), the pH values decreased rapidly, which obviously influenced the efficacy of oriented LA bioconversion of the system. It was demonstrated that the pH of the fermentation system is one of the main parameters affecting LA bioconversion. In this study, it was found that the E. mundtii-inoculated groups (Groups G and H; Fig. 2) exhibited equally poor

in real time.



**Fig. 2. Effects of inoculation and saccharification of LA production from FW without pH regulation.** (E) Group E, without saccharification, non-inoculation, pH adjusted to initial 6.8; (F) Group F, saccharification, non-inoculation, pH adjusted to initial 6.8; (G) Group G, without saccharification, inoculation, pH adjusted to initial 6.8; (H) Group H, saccharification, inoculation, pH adjusted to initial 6.8.

As free acid establishes feedback inhibition, strains cell membranes, metabolic systems, and substrate transport pathways are impaired, and LA concentration and yield are relatively low when pH is maintained at low levels. Table 2 illustrates LA production from FW under different conditions in this study. Literature reports regarding LA production from FW in recent years are summarized in this study. Numerous studies have reported on the bioconversion of FW to LA. We concluded that the LA concentration ranged from 12.9 to 94.0 g/L, and the LA yield ranged from 0.09 to 0.94 g/g in reported works. In contrast, in the present study, the highest LA production (115 g/L) was obtained in Group D (Table 2) with a high LA yield (0.97 g-LA/g-total sugar), which was much higher than that reported in the literature. The high LA concentration in the fermentation broth has several significant advantages, including a reduction in the volume of the fermenter, lower energy consumption for downstream separation and purification, and reduced water consumption and wastewater formation. In conclusion, the experimental open FW fermentation for LA production described in this study has the advantages of a short fermentation time and high LA yield, which offer potential wide popularization and application prospects.

#### <u>Mass balance in oriented LA bioconversion from</u> FW

Mass balance analysis of the FW resource recovery process is useful for evaluating the economic efficiency of the process and the design of each procedure for the entire organic solid waste treatment. In this study, the mass balance calculation in the oriented bioconversion of FW to LA was mainly achieved by calculating the masses of substances entering and leaving the system in different treatment steps in the beginning  $\rightarrow$  process end stages. It mainly included masses of FW, glycosylase, exogenous inoculation strain, and LA in the fermentation broth entering and leaving the treatment system. To facilitate the calculation, substrate and products involved in the fermentation reaction were scaled up to the pilot scale in this mass balance calculation; that is, the FW treatment load was 100 ton-FW/d. In the calculation of FW fermentation to LA, the amount of fermentation substrate added.

fermentation conditions, and metabolites produced were based on a FW to water ratio of 1:0.5 (m/v). The saccharified substrate with the addition of 10 % (v/v) *E. mundtii* and continuous real-time pH control at 6.8 were set as the conditions for mass calculations. The specific mass calculations are presented in Fig. 3. From mass balance analysis, it indicated this process treated 100 t FW per day that would produce 128.7 t and 21.5 t of saccharified liquid and saccharified solid residue,

respectively. Finally, approximately 15.1 t LA was produced per day after 120 h of oriented LA bioconversion, and LA production accounted for 11.7 % of the mass of the saccharified liquid.

In summary, this fermentation process can effectively recover LA while realizing FW treatment, which is a more reasonable and practical process for FW resource recovery than conventional FW disposal.



Fig. 3. Mass balance of efficient oriented LA bioconversion from FW in open fermentation mode.



**Fig. 4.** Gas emissions and fermentation products in different open bioconversion modes with FW as substrate. (a) oriented lactic acid bioconversion, *Enterococcus mundtii* inoculation, pH control at 6.8,43°C; (b) anaerobic fermentation without inoculation, without pH control, at 37°C; (c) ethanol production, yeast addition, without pH control, 35°C.

#### <u>Biological carbon fixation evaluation in oriented LA</u> <u>bioconversion from FW</u>

In this study, CO<sub>2</sub> emissions during different biocon-version processes (oriented LA conversion with inoculation, bioconversion without exogenous inoculation, and ethanol conversion with yeast) involving FW were carried out under open and saccharified conditions. As shown in Fig. 4, open batch fermentation of FW inoculated with E. mundtii produced only 13.2 mL H<sub>2</sub> and 3.1 mL CO<sub>2</sub>, with LA reaching a maximum concentration of 109 g/L at 96 h, with acetic acid and ethanol reaching a maximum concentration of 7.78 g/L and 7.38 g/L at 48 h and 60 h, respectively (Fig. 4a). Open batch fermentation of FW without inoculation produced 5,353.1 mL CO<sub>2</sub>, with LA reaching a maximum concentration of 29.0 g/L at 96 h, with acetic acid and ethanol reaching maximum concentrations of 3.54 g/L and 47.2 g/L at 120 h and 96 h, respectively (Fig. 4b). Open batch fermentation of FW using additional yeast produced 5,417.3 mL of CO<sub>2</sub>, ethanol as the main product reaching a maximum level of 53.5 g/L after 96 h, LA and acetic acid reaching a maximum concentrations of 18.8 g/L and 3.48 g/L at 72 h and 60 h, respectively (Fig. 4c). The *E. mundtii* used in batch fermentation is a homolactic LAB, and the reaction equation is shown in Eq. (1). Almost all of the substrate carbohydrates were converted to LA, and there was nearly no loss of carbon sources during microbial metabolism compared with heterolactic fermentation reaction (2). The substrate carbon source is inevitably converted to CO<sub>2</sub>, during other types of anaerobic fermentation.

 $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH(1)$ 

 $C_6H_{12}O_6 \rightarrow CH_3CHOHCOOH + CH_3CH_2OH + CO_2(2)$ 

The  $CO_2$  emission per ton of FW was 0.010 kg/t with the open and efficient oriented LA bioconversion process, compared to 21.4 kg per ton of FW with indigenous microbes anaerobically without inoculation, and 21.7 kg per ton of FW with conventional open study could convert the organic carbon sources in FW into LA maximally, fix the fermentable carbon source into LA, retain it in the fermentation product, and reduce the possibility of a large amount of carbon source being converted into CO<sub>2</sub> and emitted into the environment. Eventually, the efficient oriented LA bioconversion process could enable the establishment of a novel, green and low-carbon FW resource treatment approach, which could reduce CO<sub>2</sub> emissions by 2,100-fold lower compared with traditional anaerobic acidification and ethanol fermentation processes.

#### CONCLUSIONS

In this study, a highly efficient biological LA production process was established using saccharined FW as a raw material in open mode with the addition of *E. mundtii* under continuous real-time pH control at 6.8. *E. mundtii* was found to adapt to a complex FW substrate, which could occupy the dominant strain in the open system. The oriented LA bioconversion exhibited the capacity for biological carbon fixation by reducing  $CO_2$  emissions by at least 21 kg per ton of FW under anaerobic conditions.

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ethanol fermentation, both of which had similar and higher CO<sub>2</sub> emissions. Therefore, the open and highly efficient oriented LA bioconversion technology in this Program of China (Grant NO. 2022YFE0118800), the National Natural Science Foundation of China (Grant NO. 22276012), the Ecological Environment Science & Technology Project of Anhui Province (Grant NO. 2023hb0015).

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# SHORT-TERM HIGH TEMPERATURE PRETREATMENT TO REDUCE GASEOUS EMISSION AND ADVANCE HUMIFICATION IN FOOD WASTE DIGESTATE COMPOSTING: PERFORMANCE AND MECHANISMS

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#### Abstract

This study investigates the effects of high-temperature pretreatment on the composting process and gas emissions from food waste digestate (FWD). Before composting, high-temperature pretreatments of FWD were conducted at various temperatures (70, 80, and 90 °C), times (2, 4, and 6 h), and ventilation rates (0, 0.1, and 0.2)m<sup>3</sup>·min<sup>-1</sup>·m<sup>-3</sup>). The evaluation assessed composting efficiency, gas emissions, and differences in microbial communities across the experimental groups. The results indicate that high-temperature pretreatment significantly enhances compost humification and reduces gas emissions. In conclusion, high-temperature pretreatment fosters a unique microbial community structure, enhancing the maturation of FWD compost and reducing gas emissions.

#### Keywords

Composting; High-temperature pretreatment; Food waste digestate; Gaseous emission reduction; Microbial community structure

#### 1. Introduction

According to a report by the Food and Agriculture Organization, the world produces 1.3 billion tons of food waste (FW) annually, accounting for one-third of total food production [1]. Anaerobic digestion converts FW into CH<sub>4</sub>-rich biogas, thus promoting waste reduction and the production of green energy. However, this process inevitably produces approximately 20% byproduct, referred to as FWD. FWD contains significant amounts of undegraded organic matter (OM), nutrients, and minerals [1,2], making it promising for soil improvement and other applications [3]. However, FWD typically exhibits weak alkalinity (pH 7.5-9), high ammonia nitrogen levels (800-6000 mg·kg<sup>-1</sup>) [1], high electrical conductivity (EC) (average 5.33  $mS \cdot cm^{-1}$ ), high moisture content (69.8-96.4%), and a poor physical structure. These properties can result in the emission of odorous gases and greenhouse gases (GHGs) when FWD is directly applied to soil, and they may also have toxic effects on plants [3]. Therefore, further stabilization treatment of FWD is necessary.

Composting can convert unstable OM in FWD into stable humic substances (HS), thereby reducing plant toxicity, promoting nutrient recycling, and supporting circular economic development [4]. However, traditional composting features a long maturation cycle and low degrees of humification. Additionally, the degradation of nitrogen and sulfur-containing substances not only generates unpleasant odors but also results in nutrient loss [2]. Additionally, the anaerobic degradation of FW produces various foul-smelling substances, and the resulting digestate typically exhibits high ammonia nitrogen levels. FWD has a higher concentration of odorous gases before composting than other substrates.

In response, this study conducts high-temperature pretreatment of FWD under various conditions to investigate its effects on the physicochemical properties, gas emissions, and microbial communities during composting. The objectives of this study are: (1) to reveal the effects of high-temperature pretreatment on promoting the composting maturity of FWD and reducing gas emissions; (2) to identify the optimal conditions for high-temperature pretreatment; and (3) to elucidate the mechanisms by which high-temperature pretreatment positively influences the composting process and the quality of FWD.

#### 2. Materials and methods

# 2.1. Composting materials and high-temperature pretreatment

The FWD for this study was obtained from a FW treatment plant in Chongqing, China, with birch wood chips employed as the conditioning material. Before high-temperature pretreatment, FWD and birch wood chips were mixed homogeneously in a dry weight ratio of 8:1(dry weight). The high-temperature pretreatment temperatures were set at 70, 80, and 90 °C . Ventilation rates were established according to the Chinese standard "Technical Specification for Composting of Municipal Solid Waste" (CJJ 52-2014), with values of 0, 0.1, and 0.2 m<sup>3</sup>·min<sup>-1</sup>·m<sup>-3</sup>. The pretreatment

durations were 2, 4, and 6 hours, respectively. Throughout these pretreatment periods, the moisture content of the material was maintained within the optimal range for microbial activity (50-60%) [4]. As shown in Table 1, an orthogonal experimental design was constructed based on three factors, each with three levels.

Table 1 Orthogonal Experimental Design

|     | Trea         | Crown |  |        |
|-----|--------------|-------|--|--------|
| No. | Temperature/ | Time  | Ventilation/                                       | oroup  |
|     | °C           | /h    | m <sup>3</sup> ·min <sup>-1</sup> ·m <sup>-3</sup> | naming |
| 1   | 70           | 6     | 0.1  | 761    |
| 2   | 70           | 2     | 0  | 720    |
| 3   | 70           | 4     | 0.2  | 742    |
| 4   | 80           | 6     | 0  | 860    |
| 5   | 80           | 2     | 0.2  | 822    |
| 6   | 80           | 4     | 0.1  | 841    |
| 7   | 90           | 6     | 0.2  | 962    |
| 8   | 90           | 2     | 0.1  | 921    |
| 9   | 90           | 4     | 0  | 940    |

Note: In the text, the above experimental groups are collectively referred to as the HTP group.

#### 2.2. Composting Experiment

After high-temperature pretreatment, the FWD was removed from the pretreatment device and placed in a well-ventilated area to cool naturally, as shown in Table 1. The FWD was then transferred to a 15 L plastic bucket to initiate the composting phase. Alongside the nine treatment groups previously mentioned, the group that underwent composting without high-temperature pretreatment is designated as CK. Each treatment group included three parallel experiments, with all FWD composting experiments lasting 15 days. Samples were collected on days 1, 4, 8, 10, and 15 of the composting process from the upper, middle, and lower sections of the reactor to determine physicochemical properties and microbial communities.

#### 2.3. Analytic methods
During the composting process, the germination index (GI) was measured following the methods described by Xu et al. [4]. The concentrations of HS, humic acid (HA), fulvic acid (FA), and DP were determined using the methods described by Zhu et al. [5].

The determination of hydrogen sulfide ( $H_2S$ ), dimethyl sulfide ( $Me_2S$ ), and dimethyl disulfide ( $Me_2SS$ ) was conducted using the method described by Wang et al. [2]. The quantification of carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), nitrous oxide ( $N_2O$ ), and ammonia ( $NH_3$ ) followed the procedure outlined by Cheng et al. [3].

The sequencing targeted the bacterial 16S rRNA V3–V4 region, utilizing primers 338F and 806R (sequences: 5'–ACTCCTACGGGAGGCAGCAG–3' and 5'–GGACTACHVGGGTWTCTAAT–3'). T he sequencing was performed on the PE300 plat form (Illumina, USA). Bioinformatics analysis of amplicon sequence variants was conducted usin g the Majorbio Cloud Platform (<u>https://www.majorbio.com</u>).

2.4. Statistical analyses: Statistical analysis was performed using SPSS 13.0 software, and differences between treatments were assessed using one-way ANOVA. Multiple comparisons were conducted using Duncan's method ( $\alpha = 0.05$ ).

#### 3. Results and discussion

# **3.1. Effect of high-temperature pretreatment on physicochemical properties and compost quality**

According to the Chinese organic fertilizer standard NY525-2021, when GI greater than 70% indicates that the compost is mature. Furthermore, some researchers indicate that a GI exceeding 80% is required for compost products to be free of phytotoxicity [4]. As shown in Fig. 1a, the GI of all treatments gradually increased throughout the composting process. The 822 and 921 treatments achieved maturity first on the 10th day of

composting, with GI of 82.63 and 76.09%, respectively, significantly higher than those of the other treatment groups. Subsequently, the GI of these two groups increased rapidly, reaching 131.74 and 127.79% at 15 days, respectively. Even at 15 days, the GI of the CK, 720, 860, and 940 treatment had reached 80%. The groups not yet high-temperature pretreatment groups lacked during ventilation the pretreatment process. Ventilation during high-temperature pretreatment significantly influences the subsequent composting process of FWD. Due to the relatively poor composting effects of the 720, 860, and 940 treatment groups, no further detailed data analysis was performed on these groups in the later stages.

HS is a macromolecular organic compound produced by the microbial decomposition of OM during composting. It is an important indicator of compost humification, comprising FA and HA [6]. While HS content typically increases in most studies [5,7], it gradually decreased in this study (Fig. 1b). The rapid decline of FA and the slow increase of HA, as shown in Fig. 1c and Fig. 1d, support this inference. FA is a simple molecule rich in phenolic hydroxyl and carbonyl groups. It can be transformed into more stable substances, such as HA, and serves as a carbon source for microbial metabolism [6]. During the initial stage, the concentrations of FA and HA were comparable. However, during the first 8 days of composting, the concentration of FA rapidly decreased, likely due to its instability and subsequent microbial metabolism. In contrast, the more stable HA concentration remained relatively constant, contributing to the rapid decline of HS during the first 8 days. After 8 days, FA concentration continued to decline, while HA concentration began to increase, slowing the downward trend of HS. Comparing the three parameters among different treatment groups, FA concentration in the CK group was significantly higher than in the HTP group (p <0.05). Conversely, HA and HS concentrations were significantly lower in the CK group (p < 0.05). This indicates that high-temperature pretreatment significantly enhanced the humification of the composting materials. The type of substrate significantly influences these parameters, causing their content to fluctuate and making horizontal comparisons across different groups challenging. In contrast, the DP, defined as the ratio of HA to FA,

is more suitable for evaluating compost humification [8]. It is widely recognized that a degree of stability and maturity in the composting process is achieved when the DP exceeds 1.9 [7]. As shown in Fig. 1e,

the DP of each treatment group increased rapidly after day 8. By day 12, DP values for all HTP groups exceeded 1.9, reaching 2.59-2.78 by day 15. In contrast, the CK group did not exceed a DP value of 1.9 until the end of the composting process. The DP of the HTP groups was 28.51-37.97% higher than that of the CK group, indicating that high-temperature pretreatment enhances HS stability and promotes the humification process during composting [5].



Fig. 1. Changes in GI (a), HS (b), FA (c) and, HA (d) and DP (e) during composting.

# 3.2. Effect of high-temperature pretreatment on odor gas and greenhouse gas emissions during composting process

The primary odorous gases monitored in FWD compost were NH<sub>3</sub>, H<sub>2</sub>S, Me<sub>2</sub>S, and Me<sub>2</sub>SS. NH<sub>3</sub> emissions is the primary contributor to N loss during composting and the main odorous gas produced. In this study, cumulative NH<sub>3</sub> emissions ranged from 1465.01 to 2127.32 mg·kg<sup>-1</sup>, followed by Me<sub>2</sub>SS (28.09 to 45.46 mg·kg<sup>-1</sup>), Me<sub>2</sub>S (5.48 to 10.27 mg·kg<sup>-1</sup>), and H<sub>2</sub>S (1.30 to 2.17 mg·kg<sup>-1</sup>).

Fig. 2a and Fig. 2b illustrate the daily and cumulative emissions of NH3 for each treatment throughout the composting process. All treatments exhibited significant NH<sub>3</sub> emissions during the first 5 days of composting. Subsequently, NH<sub>3</sub> emissions gradually decreased, likely due to a drop in temperature within the compost mass and the consumption of OM. High-temperature pretreatment significantly reduced cumulative NH<sub>3</sub> emissions, with the 822 group showing a 16.9% reduction compared to the CK group (p < 0.05). This reduction may result from the selective pressure exerted by high-temperature pretreatment on thermophilic nitrifying bacteria, which enhances the conversion of NH4+-N to NO3--N [2]. Fig. 2c presents the daily emissions of H<sub>2</sub>S during the FWD composting process. Significant variations in initial H<sub>2</sub>S emission rates were observed among the treatment groups due to differences in treatment conditions (p < 0.05). H<sub>2</sub>S emission was primarily concentrated during the thermophilic stage of composting, peaking on the day 3. This may result from the intense biodegradation of OM in the early composting stages, leading to an anaerobic environment that promotes the activity and growth of sulfate-reducing bacteria [10]. High-temperature pretreatment significantly reduced cumulative H2S emissions during the composting process (Fig. 2d). Compared to the CK group, H<sub>2</sub>S reductions in the HTP group ranged from 11.10 to 36.06%. This may

be attributed to high-temperature pretreatment, which decreases the water content of composting materials, reduces the formation of anaerobic environments during the composting process, and inhibits the activity of SRB [9].

In addition to H<sub>2</sub>S, Me<sub>2</sub>S and Me<sub>2</sub>SS are two other significant sulfur-containing gases produced during the FWD composting process. Due to their low odor thresholds, even at minimal concentrations, these gases can cause discomfort to humans [9]. Me<sub>2</sub>S and Me<sub>2</sub>SS may be produced from the degradation of sulfur-containing amino acids in the composting material and from the methylation of H<sub>2</sub>S or methanethiol [9]. Fig. 2e shows that Me<sub>2</sub>S emissions changed dynamically during the first 12 days of composting. This change may result from the continuous interconversion between H2S and Me2S through methylation and demethylation processes [9]. Given that high-temperature pretreatment has reduced H<sub>2</sub>S generation (Fig. 2d), it may also inhibit the methylation process, thereby decreasing Me<sub>2</sub>S production. Fig. 2f presents cumulative emission data supporting this inference. It shows that cumulative Me<sub>2</sub>S emission in the CK group is highest at 10.27 mg·kg<sup>-1</sup>, while the HTP group exhibits a 46.63% reduction to 23.56 mg·kg<sup>-1</sup>. This finding demonstrates that high-temperature pretreatment effectively reduces the production and emission of Me<sub>2</sub>S. In contrast to the previously mentioned sulfur-containing gases, Me<sub>2</sub>SS production primarily results from the microbial decomposition of cysteine [9]. Fig. 2g shows that Me<sub>2</sub>SS levels remain high from days 1 to 5 of composting, with most treatment groups reaching maximum emissions on day 3. Significant differences in Me<sub>2</sub>SS emission levels were observed among the various treatments (Fig. 2h). However, high-temperature pretreatment significantly decreased the production and emission of Me<sub>2</sub>SS gas in the HTP group, with emissions in the 822 group

reduced by 32.76% (p < 0.05) compared to the CK group.

During the FWD composting process, GHGs such as  $N_2O$ ,  $CH_4$ , and  $CO_2$  are generated alongside odorous gases. As illustrated in Fig. 3, the trends in gas emissions and cumulative GHG emissions across the treatment groups were generally similar, with higher emission levels observed in the early stages of composting, which gradually decreased and stabilized as the process progressed. As illustrated in Fig. 3a,  $CO_2$  emissions gradually decreased as

composting progressed, beginning on day 6 with relatively lower dynamic emission levels. This decline is attributed to the reduced availability of OM, a phenomenon confirmed by multiple studies [4,11]. By the end of composting, all HTP groups, except for 761, significantly reduced cumulative CO<sub>2</sub> emissions compared to the CK group (p < 0.05), with reductions ranging from 20.42 to 37.04%. The  $CO_2$ emissions decrease in suggests that high-temperature pretreatment may enhance carbon fixation during composting to synthesize HS [12].



Fig.2. Odorous gases during the composting process: daily NH<sub>3</sub> emissions (a), cumulative NH<sub>3</sub> emissions (b), daily H<sub>2</sub>S emissions (c), cumulative H<sub>2</sub>S emissions (d), daily Me<sub>2</sub>S emissions (e), cumulative Me<sub>2</sub>S emissions (f), daily Me<sub>2</sub>SS emissions (g), and cumulative Me<sub>2</sub>SS emissions (h).

CH<sub>4</sub> emissions primarily occurred during the initial stages of composting; subsequently, from day 7 onwards, emissions dropped below the detection limit (Fig. 3b). The early peak in CH<sub>4</sub> emissions was mainly due to the high abundance of methanogens in the FWD, while the rich OM at the start of composting facilitated rapid microbial proliferation, resulting in anaerobic conditions [12]. Fig. 3d shows that cumulative CH<sub>4</sub> emissions in the HTP group were reduced by 4.68 to 17.12% compared to the CK group, with the 822 treatment exhibiting a decrease of 20.28 mg·kg<sup>-1</sup> in CH<sub>4</sub> emissions relative to CK. In

contrast to the short-term rapid release of CH<sub>4</sub>, N<sub>2</sub>O emissions remained relatively high during the week prior to composting (Fig. 3c). Subsequently, N<sub>2</sub>O emissions gradually decreased and stabilized. By the end of composting, cumulative N<sub>2</sub>O emissions in the CK group were highest at 69.02 mg·kg<sup>-1</sup>. In contrast, N<sub>2</sub>O emissions in the HTP group were only 58.99 mg·kg<sup>-1</sup>, representing a reduction of 14.54% (p < 0.05). High temperatures may inhibit denitrifying bacteria, contributing to the reduction in N<sub>2</sub>O emissions observed in the HTP group [12].



Fig. 3. Daily and cumulative emissions of GHGs during composting: CO<sub>2</sub> (a), CH<sub>4</sub> (b), and N<sub>2</sub>O (c), along with total GHG emissions (d) and cumulative GHG emissions (e).

### **3.3 Analysis of microbial communities in compost under high-temperature pretreatment**

The differences in community diversity and richness among the treatments were characterized using the Shannon and Chao1 indices [13]. Overall, high-temperature pretreatment reduced the diversity of microbial communities in compost. The Shannon index for each treatment group was ordered as follows: 921 > CK > 962 > 841 > 742 > 822 > 761(Fig. 4a). This reduction in diversity may be attributed to the inactivation of certain indigenous microorganisms due to high temperatures exceeding 70 °C during pretreatment [14]. However, the Chaol index ranking was as follows: 742 > 841 >962 > 921 > 822 > CK > 761 (Fig. 4b), indicating that high-temperature pretreatment generally increased the microbial community richness in compost. The thermophilic environment eliminated heat-sensitive microorganisms, further reducing overall community diversity. However, it created a more favorable environment for the growth and reproduction of selected microorganisms [13], which may explain the increase in their richness.

The  $\boldsymbol{\beta}$  diversity further illustrates the impact of

high-temperature pretreatment on the overall microbial community [6]. Microbial distances at the genus level among different treatment groups were calculated using the weighted\_Unifrac distance, and principal coordinates analysis (PCoA) was employed to visualize the distribution of bacterial communities, as shown in Fig. 4c. PCoA1 and PCoA2 explained 63.37% and 9.33% of the total variation in the bacterial community, respectively. The Figure shows that the samples can be clustered into two categories

(p < 0.001), with the CK group forming a distinct category and the HTP group forming another. This indicates high-temperature that pretreatment significantly impacts the microbial community. Although the HTP group is more clustered than the CK group, significant differences remain among the various HTP indicating groups, that conditions high-temperature pretreatment also influence the bacterial community structure.



Fig. 4. Effects of high-temperature pretreatment on bacterial communities were analyzed through assessments of bacterial diversity using the Shannon and Chao1 indices (a and b), as well as PCoA (c). Significant differences in microbial communities were examined at the phylum (d) and genus (e) levels.

As illustrated in Fig. 4d, significant differences were observed in the abundance of five phyla: Proteobacteria, Actinobacteriota, Firmicutes, Bacteroidota, and Gemmatimonadota, between the CK and 822 groups (p < 0.05). Among these, the relative abundances of Proteobacteria and Bacteroidota in group 822 reached 66.08% and 15.63%, respectively, whereas in CK, these values were only 37.77% and 8.43%. Previous studies have indicated that Proteobacteria play a crucial role in

nutrient cycling during the composting process and are associated with compost maturity [13]. In contrast, *Bacteroidota* primarily contribute to the degradation of lignocellulose in compost, promoting the production of HS precursors [3]. Thus, the enrichment of these two microbial phyla may be linked to the rapid humification and high maturity observed in 822 group.

Further analysis at the genus level of microbial differences between group 822 and CK revealed that

the proportion of Pseudomonas in 822 (29.54%) was significantly higher than in CK (5.51%) (Fig. 4e). Studies indicate that Pseudomonas possesses nitrogen-fixing abilities and can inhibit NH<sub>3</sub> release [15]. The relatively high proportion of Pseudomonas is consistent with findings that high-temperature pretreatment promotes nitrogen retention in the FWD system composting (Section 3.2.). Sphingobacterium, Myroides, and Flavobacterium exhibited significantly higher abundances in the HTP group (p < 0.05). Previous studies indicate that Sphingobacterium is primarily present during the mature stage of composting and promotes the formation of stable HS [10]. Myroides exhibited the strong ability of the degradation of small molecular substances, such as glycolysis, starch-hydrolyzing, and pectin-degrading functions, contributing to the prolonged thermophilic phase and the increased enzymatic activities (i.e., cellulase, urease, and protease) [16]. Flavobacterium has also been reported to enhance HS formation [5]. High temperatures significantly enhance the abundance of humus-promoting microorganisms in the composting system.

#### 4. Conclusions

High-temperature pretreatment effectively enhances the maturation of FWD composting and reduces gas emissions. Among the three treatment conditions, the effects of temperature and ventilation rate on composting outcomes are more significant than those of treatment time. Under the optimal pretreatment conditions, specifically a temperature of 80 °C, a ventilation rate of 0.2 m<sup>3</sup>·min<sup>-1</sup>·m<sup>-3</sup>, and a treatment time of 2 hours, the composting process was shortened by 33.33% compared to the CK, while the DP increased by 37.79%. The reduction rates of odorous gases, including NH<sub>3</sub>, H<sub>2</sub>S, Me<sub>2</sub>S, and Me<sub>2</sub>SS, were 16.90, 21.82, 41.18, and 32.79%, respectively. Similarly, the reduction rates of GHGs, including CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, were 20.42, 17.12, 14.54%. respectively. and High-temperature

pretreatment can foster a unique microbial community structure, which is a key factor in its effectiveness for enhancing degradation and reducing emissions during FWD composting.

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# Plastic Materials by Agricultural Commodity Research on Material Flow

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In recent years, many studies have been conducted on the proper disposal of waste plastics discharged from the agricultural sector. However, there have not been enough studies on the amount of plastic materials used and discharged, focusing on the detailed classification of plastic materials by agricultural product category. In this study, we attempted to estimate the material flow of plastics used in agricultural products by classifying them into the following categories: fruits and vegetables, leafy vegetables, root vegetables, and cereals.

#### Introduction

In recent years, the recycling of plastic resources has been attracting attention in Japan and abroad. In the agricultural field, plastic materials are widely used for plastic greenhouses, mulch sheets, insect nets, etc. Plastic materials are indispensable for growing crops, especially for horticultural facilities. Therefore, many studies have been conducted on waste plastics discharged from the agricultural field. In particular, there have been many studies on the treatment stage of waste plastics from agriculture, and Takeya<sup>1)2)</sup> has investigated the current status of collection, treatment, and recycling of waste plastics from agriculture in Japan and overseas, and clarified the international resource cycle of waste plastics from agriculture in East Asia and the associated difficulties in managing an appropriate treatment system. Kuboi et al. Kuboi et al.<sup>3)4)</sup> clarify the current severe

situation of reclamation of agricultural waste plastic and its effective use as roadbed material. Nishinomiya et al.<sup>5)</sup> investigate the production of fuel pellets from agricultural waste plastic and agricultural residues. The Ministry of Agriculture, Forestry and Fisheries (MAFF) has published the status of horticultural facilities  $(R.4)^{6}$ . According to this survey, the total amount of agricultural waste plastic discharged in FY 2020 was 101,312 tons nationwide, of which 75,793 tons was from horticultural crops (vegetables, flowers, and fruit trees), 25% from other crops (rice cultivation and field crops that do not fall under horticultural crops), and the remaining 25% from other crops (rice cultivation and field crops that do not fall under horticultural crops). The amount of emissions from other crops (rice and field crops that do not fall under horticultural crops) is estimated to be 25,518 tons. However, even among horticultural crops, the amount of plastic used and emitted is expected to be different because the cultivation methods differ greatly among vegetables, such as fruiting vegetables, leafy vegetables, and root crops.

As can be seen from the above examples of previous studies, there have been many studies on the treatment and effective utilization of agricultural plastics after they are discharged as waste. However, there are no examples of studies that have investigated the classification of agricultural plastics into stock-type plastics, which are installed on farmland as plastic greenhouses, and flowtype plastics, such as plastic containers used for fertilizers and pesticides, before they are discharged as waste. If we can estimate the intensity of use and discharge of agricultural plastic materials per unit area by crop category and by type of plastic material, we can consider the appropriate disposal plan of agricultural plastic materials in a more detailed unit according to the cultivation characteristics of each agricultural product and the agricultural characteristics of each region.

In order to contribute to the solution of the abovementioned problems, this study focused on four different crop categories of agricultural crops: fruiting vegetables, leafy vegetables, root crops, and cereals, and estimated the annual plastic use per crop area by classifying them into stock-type plastics and flow-type plastics, as well as the amount of waste plastic emitted from both types of crops. The amount of waste plastic emitted from both types of plastic was also estimated.

#### **Research Methodology**

#### (1) **Questionnaires and Interviews**

In this study, a preliminary survey was conducted at the Fukuoka City Agricultural Cooperative West Green Center to develop a questionnaire to estimate the amount of agricultural plastic materials used and emitted per crop area by crop type. The survey was conducted at the Nishi Green Center of the Fukuoka City Agricultural Cooperative Association to obtain information on the types of agricultural plastic materials used by each product category. In order to increase the effective response rate, we discussed the questionnaire format with the cooperative staff and modified the questionnaire as necessary to make it easier for the respondents to respond.

Subsequently, a questionnaire survey was conducted among farmers in the five areas of Imajuku, Susenji, Motooka, Imazu, and Kitazaki in Fukuoka City's Nishi Ward under the jurisdiction of the Fukuoka City Agricultural Cooperative West Green Center in order to quantitatively understand the specific amount of plastic materials used and emitted for agricultural use. The target crops were strawberries, a fruiting vegetable cultivated in greenhouses; soft vegetables, a leafy stem vegetable cultivated in greenhouses; radishes, a root vegetable cultivated in the open; and paddy rice, a grain grown in paddy fields. The reason for selecting these four crops for the study is that they are cultivated in different ways and use or discharge different types of plastic materials. Crops representative of each cultivation type were selected from those that cooperated in the survey.

The questionnaire survey was conducted on farmers who gathered to participate in the agricultural commodityspecific subcommittees organized by the Fukuoka City Agricultural Cooperative West Green Center. The meetings are held regularly to discuss sales performance, market trends, production measures, and other issues. Table 1 shows the crop categories, the number of valid responses, the date and time of the survey, and the management style of the farmers. The number of valid responses was 20 for strawberry, 10 for soft vegetables, 4 for radish, and 8 for paddy rice. All the respondents were private farmers except for the radish farmers, and only the radish farmers were company-owned farmers. Although the number of valid responses for radish was small (4), it was considered that there was no significant difference in the statistical reliability of the responses from the other individual operators because of the relatively large scale of their operations. The breakdown of soft vegetables was as follows: shungiku (11 cases), komatsuna (7 cases), spinach (4 cases), mizuna (1 case), and kusinsai (1 case). Since these crops have a similar cultivation pattern and there is no difference in the amount of plastic materials used and emitted for agricultural use, they were unified as soft vegetables.

Table-1: Basic Information on Questionnaires Conducted in

| the Item-Specific | Subcommittees |
|-------------------|---------------|
|-------------------|---------------|

| Crop               | Crosse      | Valid         | Date and   | Type of      | Type of     |  |
|--------------------|-------------|---------------|------------|--------------|-------------|--|
| Categories         | Crops       | Responses     | Time       | Business     | Cultivation |  |
| Fruiting           | Strawberry  | 20            | 2023/11/10 | Indi vi dual | Greenhouse  |  |
| Vegetables         | 2           |               |            |              |             |  |
| Leafy Stem         | Soft        | 10            | 2023/11/25 | Individual   | Greenhouse  |  |
| Vegetables         | Vegetables  | 10 2020/11/25 | marriaam   | Greennouse   |             |  |
| Root<br>Vegetables | Radish      | 4             | 2023/11/10 | Coporate     | Open-Field  |  |
| Cusing Daddy Diss  |             | 6             | 2023/10/22 | Individual   | Open Field  |  |
| Grains             | I auuy Kite | 0             | 2023/10/22 | muiviuuai    | Open-Fieru  |  |

# (2) <u>Methods for Estimating The Use and Emission</u> <u>Intensity of Plastics of Agricultural Origin</u>

First, through interviews and questionnaires, we investigated the acreage of the crop of the study target, the type, size, annual number of plastic materials used to cultivate the target crop, and the disposal interval (average duration of use). Next, the annual quantity of plastic materials used was multiplied by the weight intensity per unit of quantity used, and then summed for each material to convert it into the annual quantity used. Finally, the annual consumption was estimated by dividing the total amount of plastic materials used by the

area planted to the crop. The annual emission intensity was calculated by dividing the annual consumption of each plastic material by the number of years between the disposal of each material, and then summing the emissions of each material to obtain the annual emission. Finally, the emissions intensity was obtained by dividing the emissions by the crop area.

The amount of plastics used was defined as stock-type agricultural plastics, which are installed on farmland as agricultural materials, such as plastic greenhouses and mulch sheets. The amount of plastics used in agricultural fertilizers and pesticides is defined as flow-type agricultural plastics, and the amount of each was calculated. In general, material flow analysis is defined in terms of time and space<sup>7)</sup>. For example, one year is treated as a unit of time, and inputs, outputs, and emissions are treated as flows, and accumulations are treated as stocks. On the other hand, it should be noted that in this study, as mentioned above, stock-type and flow-type materials are classified according to their intended use. The classification criteria and applicable materials are shown in Table 2.Plastics contained in coated fertilizers were excluded from the study because it was not possible to obtain a sufficient number of samples to estimate the stock and flow volumes.

Table-2 Material Classification in Plastic Use

|   |                            | Classification Criteria                                      | Relevant Materials                    |  |
|---|----------------------------|--|---------------------------------------|--|
| ſ |                            | Stool: Type Aminultynal Planting                             | Plastic Greenhouses, Mulch Sheets,    |  |
|   | 1                          | which are installed on farmland as<br>agricultural materials | Watertight Sheets, Insect Nets,       |  |
|   | 1                          |  | Seedling Boxes, Mycar Wires, Flexible |  |
|   |                            |  | Pots, Irrigation Tubes, PVC Pipes     |  |
| ſ |                            | Flow-Type Agricultural Plastics,                             | Fertilizer Bags, Liquid Fertilizer    |  |
| 2 | 2                          | which are used in agricultural                               | Containers, Pesticide Bags, Pesticide |  |
|   | fertilizers and pesticides | Containers   |                                       |  |

# (3) <u>Weight Data Measurement of Agricultural</u> <u>Plastics</u>

In this study, the weight of each type of waste plastic was

measured during the collection of agricultural waste plastic at the Fukuoka City Agricultural Cooperative West Green Center. The agricultural cooperative promotes the collection and recycling of agricultural waste plastics by subsidizing a portion of the processing fees paid by the farmers who produce the waste.

The means and standard deviations (n=3) of the plastic weights for each type of material obtained from the above study are shown in Table-3. Three samples were obtained and measured for each material. For the miker wire, irrigation tube, and PVC pipe, the samples were cut into 10-cm pieces and then converted to weight per meter. Data for materials with an asterisk (\*) in the material name were not measured in this study, but were supplemented by product information from agricultural material manufacturers, due to the inability to measure multiple weight data and the possibility of overestimation because of the large amount of mud adhering to the materials.

| Table-3 | Weight   | data c | of n | lastic | material | s for | agricult | hire |
|---------|----------|--------|------|--------|----------|-------|----------|------|
| raore 5 | ,, eight | autu c | L P  | iabtie | materian | 5 101 | aBriean  |      |

| Plastic Materials                        | Weight(g) | SD(g) | Unit             |
|--|-----------|-------|------------------|
| Greenhouses (PVC)*                       | 140       | 0     | g/m <sup>2</sup> |
| Greenhouses(PE)*                         | 97        | 0     | g/m <sup>2</sup> |
| Mulch Sheets                             | 72        | 0     | g/m <sup>2</sup> |
| Insect Nets                              | 50        | 2.9   | g/m <sup>2</sup> |
| Mycar Wires                              | 10        | 1.2   | g/m              |
| Potting Soil Bags 20L                    | 83        | 2.5   | g/bag            |
| Fertilizer Bags 20kg                     | 87        | 13.1  | g/bag            |
| Fertilizer Bags 40L                      | 83        | 7.6   | g/bag            |
| Liquid Fertilizer Containers 10L         | 725       | 97.7  | g/ite m          |
| Pesticide Containers 250mL               | 44.4      | 18.1  | g/ite m          |
| Pesticide Containers 500mL               | 82.3      | 31.5  | g/ite m          |
| Pesticide Containers 1000mL              | 103.8     | 11.7  | g/ite m          |
| Pesticide Bags 250g                      | 15        | 0     | g/bag            |
| Pesticide Bags 500g                      | 25        | 0     | g/bag            |
| Flexible Pots*                           | 88.2      | 41.2  | g/ite m          |
| Watertight Sheets*                       | 1419.8    | 512.7 | g/m <sup>2</sup> |
| Irrigation Tubes                         | 25        | 2.9   | g/m              |
| PVC Pipes                                | 491       | 32.3  | g/m              |
| Seedling Boxes(280×580×40)               | 632       | 19.5  | g/ite m          |
| PE Containers 5L*                        | 401       | 48.6  | g/ite m          |
| PE Containers 20L*                       | 1357      | 145.2 | g/ite m          |
| Shipping Materials (Radishes)*           | 35        | 0     | g/bag            |
| Shipping Materials<br>(Soft Vegetables)* | 35        | 0     | g/bag            |
| Shipping Materials (Strawberries)*       | 5.4       | 1.4   | g/bag            |

\* indicates materials with additional product information from the manufacture

#### **3. Survey Results**

# (1) <u>Agricultural Plastic Use by Crop Category and</u> <u>Emissions Intensity Estimation Results</u>

Figure-1 shows the results of the use and emission intensity of each agricultural product category obtained in this study.

Regarding the amount of stock-type agricultural plastics used per unit planted area by crop, the most common crop was strawberry (840 g/m<sup>2</sup> /year), followed by soft vegetables (320 g/m<sup>2</sup> /year) and paddy rice (2.2 g/m<sup>2</sup> /year). The use of stock-type agricultural plastics in radish cultivation was not confirmed. The unit for the amount of stock-type materials used was determined as g/m<sup>2</sup>/year by dividing the amount of stock-type materials used by the number of years between disposal intervals, in order to standardize the different number of years each material is used each year.

Regarding the amount of flow-type agricultural plastics used per unit planted area by crop type, the most common crop was strawberry at 12 g/m<sup>2</sup> /year, followed by soft vegetables at 10 g/m<sup>2</sup> /year, radish at 0.97 g/m<sup>2</sup> /year, and paddy rice at 0.33 g/m<sup>2</sup> /year.

Regarding the emissions per unit planted area by crop type, the largest amount was 350 g/m<sup>2</sup> /year for strawberries, followed by 63 g/m<sup>2</sup> /year for soft vegetables, 0.97 g/m<sup>2</sup> /year for radishes, and 0.64 g/m<sup>2</sup> /year for paddy rice. Packaging plastics are not included in the estimation of emissions because they are used by farmers, shipped with agricultural products, and then discharged by households that purchase agricultural products, and not by farmers. For the same reason, packaging plastics are not included in the material flow diagram.



Figure-1: Usage and emission intensity of plastics by category

#### (2) Strawberry Cultivation Survey Results

Figures 2 and 3 show the breakdown of stock-type and flow-type agricultural materials, respectively. Most of the materials used were stock-type materials, with watertight sheets and plastic greenhouses accounting for a large proportion.

Figure 4 shows the emission rate of agricultural plastic materials in strawberry cultivation. As for the amount and breakdown of emissions, the amount of emissions in proportion to the amount used was calculated to be very large. Plastic greenhouses account for about 54% of the total emissions. This is due to the fact that the replacement period of plastic greenhouses is one year. In fact, we confirmed that many strawberry farmers discarded plastic greenhouses at the site where waste plastic for agricultural use was collected.



Figure-2 Breakdown of stock-type materials used in





strawberry cultivation



Figure-4 Breakdown of agricultural material emissions in

strawberry cultivation

#### (3) Soft Vegetable Cultivation Survey Results

Figures 5 and 6 show the breakdown of stock-type and flow-type agricultural materials, respectively. Most of the materials used were stock-type materials, with insect nets and plastic greenhouses accounting for a large proportion.

Figure 7 shows the emission rate of agricultural plastic materials in the cultivation of soft vegetables. The amount of plastic greenhouses and watertight sheets account for a large proportion of the total discharge, but the amount of plastic greenhouses is smaller than that of strawberry cultivation. This is due to the fact that the average period of replacing plastic greenhouses in the cultivation of soft vegetables is five years. Another reason for the relatively small amount of emissions in this study is that only agricultural polyolefin film (PO) is used for soft vegetable cultivation, whereas strawberry cultivation uses agricultural vinyl and agricultural polyolefin film (PO).



Figure-5 Breakdown of use of stock-type materials in soft vegetable cultivation



Figure-6 Breakdown of use of flow-type materials in soft

vegetable cultivation



Figure-7 Breakdown of agricultural material emissions in soft vegetable cultivation

#### (4) Radish Cultivation Survey Results

Figure-8 shows the percentage of flow-type agricultural materials discharged. More than 70% of the flow-type agricultural materials were calculated to be fertilizer bags. The same is true for the use rate of flow-type agricultural materials.



Figure-8 Breakdown of agricultural material emissions in radish cultivation

#### (5) Paddy Rice Cultivation Survey Results

Figure-9 shows a breakdown of the discharge of agricultural plastic materials in paddy rice cultivation. About 50% of the emissions are from seedling boxes.



Figure-9 Breakdown of agricultural material emissions in paddy rice cultivation

#### 4. Conclusion

In this study, a survey was conducted on the use and emissions of agricultural plastic materials by agricultural commodity. The findings of this study are as follows Stock-type plastic use per unit cropland area was 840 g/m<sup>2</sup>/year for fruit vegetables, 320 g/m<sup>2</sup>/year for leafy greens, 0 g/m<sup>2</sup>/year for root crops, and 2.2 g/m<sup>2</sup>/year for cereal crops. Flow-type plastic use was 12 g/m<sup>2</sup>/year for fruiting vegetables, 10 g/m<sup>2</sup>/year for leafy greens, 0.97 g/m<sup>2</sup>/year for root crops, and 0.33 g/m<sup>2</sup>/year for cereal crops. On the other hand, the total amount of stock-type and flow-type waste plastics emitted from farmland per year was 350 g/m<sup>2</sup>/year for fruit vegetables, 63 g/m<sup>2</sup> /year for leafy stem vegetables, 0.97 g/m<sup>2</sup>/year for root vegetables, and 0.64 g/m<sup>2</sup>/year for cereal crops.

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## Ethanol-type anaerobic digestion promoted methane production and improved system stability

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#### ABSTRACT

This study configured the feed according to COD ratios of ethanol : sodium acetate : sodium propionate : sodium butyrate of 5:2:1.5:1.5 (ethanol-type anaerobic digestion) and 0:5:2.5:2.5 (control), and conducted semicontinuous anaerobic digestion (AD) experiments. The results showed that ethanol-type AD increased maximum tolerable organic loading rate (OLR) to 6.0 gCOD/L/d, and increased the methane production by 1.2-14.8 times compared to the control at OLRs of 1.0-5.0 gCOD/L/d. The abundance of the pilA gene, which was associated with direct interspecies electron transfer (DIET), increased by 5.6 times during ethanol-type AD. Ethanol-type AD improved methanogenic performance and enhanced system stability by stimulating DIET.

#### **1.INTRODUCTION**

Anaerobic digestion (AD) is a competitive approach for the management of organic waste and wastewater, because it offers a dual benefit of pollutant reduction and bioenergy recovery [1]. The AD process consists of four distinct s: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During the acetogenesis phase of AD, the conversion of propionate and butyrate into acetate is thermodynamically unfavorable [2]. Consequently, during propionate- or butyrate-type AD, the slow utilization of organic acids can easily lead to acid accumulation, thereby adversely affecting methanogenesis. Thermodynamically, the conversion of ethanol to acetate is comparatively simpler than that of propionate and butyrate.

Ethanol pre-fermentation is a pretreatment technique to produce ethanol before AD by inoculating yeast into food waste (FW) [3]. Ethanol pre-fermentation preferentially converts the carbon (mainly carbohydrates) in FW into ethanol, strengthening the pathway for ethanol production and diminishing those for propionate and butyrate production. The process is beneficial for establishing an ethanol-type AD system, which can improve the methane production efficiency and stability of AD systems [4]. However, these studies have mainly concerned with the role in ethanol pre-fermentation in alleviating acidification and improving system stability.

There are many complex organic components in FW in addition to ethanol and volatile fatty acids (VFAs). There has been no research investigating the impact of ethanol pre-fermentation on the carbon metabolism pathways.

Mediated interspecies electron transfer (MIET), dominated by interspecies hydrogen transfer (IHT), is the main electron transfer pathway in the syntrophic metabolism of anaerobic microbial [5]. Recent studies have demonstrated that ethanol-type AD reactors constructed with ethanol as a substrate not only tolerate the disturbance of acid accumulation, but also stimulate the direct interspecies electron transfer (DIET) process among syntrophic microorganisms [6,7]. Zhao et al. indicated that the conductivity of the ethanol-stimulated sludge increased considerably, and that DIET may be established between Geobacter and Methanosaeta or Methanosarcina [8]. However, previous studies have mainly investigated the promotion of DIET by ethanol as a single substrate of AD. Whether DIET is stimulated in ethanol-type AD systems constructed by ethanol prefermentation of FW remain unknown.

This study aimed to explore the influences of an ethanoltype AD system, constructed through the prefermentation of FW, on interspecies electron transfer. To more thoroughly explore the carbon metabolism pathway and avoid interference from other organic compounds, the feed was configured with COD ratios of ethanol : sodium acetate : sodium propionate : sodium butyrate of 5:2:1.5:1.5 and 0:5:2.5:2.5. Semi-continuous AD experiments simulating FW with and without ethanol pre-fermentation were conducted under the same conditions to gain insights into the impact on carbon metabolism and interspecies electron transfer, which are crucial for revealing the advantages of ethanol-type AD system.

#### 2. MATERIALSAND METHODS

#### 2.1 Experimental operation

Semi-continuous experiments were conducted using 1-L continuously stirred reactors with effective working volume of 900 mL. Two experimental groups were established: an ethanol-type AD group and a control group. The experimental conditions and the total COD

concentration of the feed were the same for two groups, but only the proportions of COD in the feed were different. The COD ratio of the reactor feed for the ethanol-type AD group was ethanol : sodium acetate : sodium propionate : sodium butyrate =5:2:1.5:1.5. The COD ratio of the control group was 0:5:2.5:2.5. A vitamin solution (10 mL/L) and a trace element solution (10 mL/L) were also added to the feed [9]. Trace element solution (mg/L): MnSO<sub>4</sub>·2H<sub>2</sub>O, 500; FeSO<sub>4</sub>·7H<sub>2</sub>O, 100; NiCl<sub>2</sub>·6H<sub>2</sub>O, 40; CoCl<sub>2</sub>·6H<sub>2</sub>O, 48; ZnCl<sub>2</sub>, 130; CuSO<sub>4</sub>·5H<sub>2</sub>O, 10; AlK(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, 10; H<sub>3</sub>BO<sub>3</sub>, 10; Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 25; CaCl<sub>2</sub>·2H<sub>2</sub>O, 100; MgCl<sub>2</sub>·6H<sub>2</sub>O, 200; EDTA, 100. Vitamin solution (mg/L): B1, 5; B2, 5; B5, 5; B6, 10; B7, 2; B12, 0.1; P-aminobenzoic acid, 5; Lipoic acid, 5; Niacin, 5; Fulvic acid, 2. The ethanoltype AD and control reactors were set up in parallel and were fed and discharged once a day. The OLR of the reactor was set at 1.0 g COD/L/d initially and gradually increased to 6.0 g COD/L/d. The experiments were conducted in a water bath set at  $37 \pm 1^{\circ}$ C. The reactors were equipped with stirring motors and stirred at a speed of 120 rpm.

#### 2.2 Analytical methods

CO<sub>2</sub> and H<sub>2</sub>S in the biogas generated during the experiment was first fully absorbed using a 3-mol/L NaOH absorption solution (with a concentration of 0.4% thymolphthalein as a pH indicator) to reduce carbon emissions. The methane produced passed through the gas pipes and the volume was measured using a gas volumetric device (AMPTS II, Bioprocess Control Co., Ltd., Sweden), which automatically recorded the measured data on a laptop computer via the internet. The concentrations of ethanol and VFAs were measured using gas chromatography (Shimadzu GC-2010plus). The corresponding relationship between COD and both VFAs and ethanol was as follows: 1.07 gCOD/g of acetate, 1.51 gCOD/g of propionate, 1.82 gCOD/g of gCOD/g of ethanol. An butyrate, and 2.67 electrochemical workstation (CHI660E, Chenhua Instrument Co., Ltd., Shanghai, China) was used to measure and analyze the cyclic voltammetry (CV) curves. Sludge conductivity was determined with a reference [8]. The conductivity of the sludge was determined using linear sweep voltammetry. The gene abundance was predicted using PICRUSt2 (v2.2.0 https://github.com/picrust/picrust2/).

#### **3. RESULT AND DISCUSSION**

#### 3.1 Effect of ethanol-type AD on methane production

Fig. 1 shows the daily methane production and average methane yield per unit of organic matter for ethanol-type AD and the control at different OLRs. During the OLR increase from 1.0 gCOD/L/d to 5.0 gCOD/L/d, the daily methane production from ethanol- type AD gradually increased from  $173.3 \pm 0.3$  mL/d to  $631.9 \pm 4.4$  mL/d

(Fig. 1a). Daily methane production from the control gradually increased from 144.6  $\pm$  3.9 mL/d to 283.9  $\pm$  0.3 mL/d as the OLR increase from 1.0 gCOD/L/d to 3.0 gCOD/L/d. As the OLR was further increased to 4.0 gCOD/L/d and 5.0 gCOD/L/d, the daily methane production of the control gradually decreased until it approached zero. During the whole AD process, the daily methane production of the ethanol-type AD was consistently higher than that of the control. At OLR of 1.0–5.0 gCOD/L/d, the daily methane production of the control.

At OLRs of 1.0, 2.0, and 3.0 gCOD/L/d, the average methane yield of ethanol-type AD (214.1  $\pm$  0.1, 160.8  $\pm$  2.2, and 145.9  $\pm$  1.4 mL/g COD-1) increased by 16.3%, 25.8%, and 44.6%, respectively, compared to the control (183.7  $\pm$  4.6, 128.4  $\pm$  1.1, and 101.2  $\pm$  0.5 mL/g COD<sup>-1</sup>) (Fig. 1b). In terms of methanogenic performance, the ethanol-type AD showed superior performance over the conventional AD (control) fed with acetate, propionate, and butyrate. The maximum OLR tolerated by the conventional and ethanol-type AD were 4.0 gCOD/L/d and 6.0 gCOD/L/d, respectively. Ethanol-type AD enhanced the AD system stability, which was associated with a higher proportion of ethanol in influent.



Fig.1 Variation in daily methane production and average methane yield per unit of organic matter.

#### 3.2 Effect of ethanol-type AD on COD degradation

The COD concentrations of VFAs in the influent and effluent sludges are shown in Fig. 2. There was no accumulation of VFAs observed within the first 30 d of AD (OLR  $\leq$  4.0 gCOD/L/d) in both the ethanol-type AD and the control. During the first 30 d, the mean COD concentration of effluent in the ethanol-type AD (487.6  $\pm$  7.2 mg/L) was 14.2% lower than that in the control

 $(568.6 \pm 2.3 \text{ mg/L})$ . The mean concentrations of acetate, propionate, and butyrate in ethanol-type AD were 287.5  $\pm$  1.9, 148.1  $\pm$  6.1, and 46.2  $\pm$  0.6 mgCOD/L, which were 13.1%, 20.0%, and 11.9% lower than that in the control  $(331.0 \pm 4.0, 185.2 \pm 0.7, \text{ and } 52.4 \pm 2.4 \text{ mgCOD/L}),$ respectively. On day 50 of AD, methane production in the control decreased to zero and the experiment ended, while ethanol-type AD continued the experiment at OLR = 6.0 gCOD/L/d (Fig. 1a). When the OLR increased to 6.0 gCOD/L/d, VFAs of the ethanol-type AD began to accumulate in large quantities. Accumulation of ethanol was only observed on days 58 and 60, and the concentration of acetate was less than that of propionate and butyrate. Therefore, the feeding ethanol in ethanoltype AD could be degraded rapidly, whereas propionate and butyrate accumulation occurred easily observed in conventional AD.



Fig.2 Variation of COD concentration in influent and effluent with time.

#### 3.3 Effect of ethanol-type AD on DIET

The redox capacity of the system was evaluated using CV curves [10]. The results showed that the peaks of the oxidation and reduction currents in ethanol-type AD showed higher values than those of control at the same scan rate (Fig.3 a). The height of the peak currents indicates the electrochemical capacity of the electroactive microorganisms and their extracellular electron transfer capacity [11]. The higher peak currents of the CV curves demonstrated that the ethanol-type AD system improved extracellular electron transfer (EET).

Fig. 3b, c shows the relative abundance of genes associated with DIET in ethanol-type AD and control. Epili and c-type cytochromes are key components involved in the exchange of electrons between syntrophic microorganisms [12]. Microbial syntrophic metabolism was severely affected after knockdown of pilA (genes coding for e-pili assembly protein) or c-type cytochrome synthesis genes in the co-culture system. There was a significant difference in the abundance of the pilA gene in the ethanol-type AD compared to the control, which was 5.6 times higher than control (P =0.002 < 0.05) (Fig. 3b). However, c-type cytochrome synthesis genes were more poorly expressed in ethanoltype AD (Fig. 3c). It was reported that the abundance of pliA in ethanol-type AD reactor was much higher than that in other types digestion reactors, but synthetic genes associated with c-type cytochromes were not regulated. Therefore, ethanol-type AD promoted DIET primarily through e-pili rather than c-type cytochromes. There is a strong correlation between the expression of e-pili produced by microorganisms involved in DIET and conductivity [13]. Thus, an increase in sludge conductivity can provide evidence for the establishment DIET among microorganisms. The electrical of conductivity of ethanol-type AD sludge (0.2359  $\pm$ 0.0010 us/cm) was 0.9% higher in comparison to the control (0.2338  $\pm$  0.0001 us/cm) (Fig. 3 d). Thus, the microorganisms of ethanol-type AD exhibited higher ability for producing e-pili, and formed an interspecies electrically connected network compared to the conventional AD.



Fig.3 (a) Cyclic voltammetry (CV) curves; (b) relative abundance of pilA genes; (c) relative abundance of Ctype cytochrome synthesis genes; (d) electrical conductivity.

#### 4. CONCLUSIONS

The results showed that ethanol-type AD increased the maximum tolerated OLR to 6.0 gCOD/L/d and methane production by 1.2–14.8 times compared to the control. The abundance of the pilA gene, which was associated with direct interspecies electron transfer (DIET), increased by 5.6 times during ethanol-type AD.

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# Study on biodegradability of trans -1,2- dichloroethylene in landfill cover under micro-aerobic environment

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#### Abstract

Methane oxidation in landfill cover creates a micro-aerobic environment crucial for the controlled removal of chlorinated hydrocarbons. This study utilized actual landfill cover soil as a biological medium to investigate the biodegradation of methane oxidation-regulated trans-1,2-dichloroethylene (t-1,2-DCE) under micro-aerobic conditions and to identify the functional microbial strains present. Oxygen concentrations were set at 0.1-1 mg/L with a 0.1 mg/L gradient and 1.0-10.0 mg/L with a 2.5 mg/L gradient. Trans-1,2-DCE was chosen as the degradation substrate. The optimal oxygen concentration for degrading trans-1,2-DCE under micro-aerobic conditions was 0.5 mg/L, achieving a 99% degradation rate. The apparent degradation rate of trans-1,2-DCE peaked at 29 µg·g<sup>-1</sup>·h<sup>-1</sup> with oxygen concentrations of 0.4 and 0.5 mg/L, increasing initially and then decreasing with the concentration gradient. The net degradation rate was 27 µg·g<sup>-1</sup>·h<sup>-1</sup>. Following the trans-1,2-DCE degradation experiment, high-throughput sequencing technology was used to analyze the samples. Methylomonas and Methylobacter were found to dominate the microbial community structure in the mulch soil. At an oxygen concentration of 0.5 mg/L, significant differences were observed, with methane primarily serving as the carbon source.

The study demonstrated that dechlorination bacteria could engage in both aerobic and anaerobic co-metabolism under micro-aerobic conditions.

**Keywords**: Micro-aerobic scale, Chloroethenes, Landfill cover soil, Methane oxidation

#### 1. Introduction

Landfilling is recognized as a cost-effective method for managing solid waste, capable of processing substantial volumes safely and thus is extensively employed globally<sup>[1]</sup>. The majority of sites contaminated with chlorinated hydrocarbons (CAHs) exist under micro-aerobic conditions, including groundwater and landfill environments<sup>[2,3]</sup>. A byproduct of the landfill stabilization process is landfill gas<sup>[4]</sup>, which is primarily composed of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and volatile organic compounds, with CAHs being a significant component<sup>[5,6]</sup>. The unregulated release of untreated landfill gases endangers the environment and public health due to the complex and highly toxic nature of CAHs, which carry risks of teratogenicity, carcinogenicity, and mutagenicity<sup>[7,8]</sup>. During the natural decomposition of waste, everyday items such as dry cleaning agents, refrigerants, and foaming agents release substantial amounts of volatile CAHs<sup>[9]</sup>. These include chlorinated olefins like 1,2-dichlorethylene (1,2-DCE), trichloroethylene (TCE), and tetrachloroethylene (PCE), as well as chlorinated aromatic hydrocarbons such as chlorobenzene (CB) and dichlorobenzene (DCBs), and chlorofluorocarbons including CFC-11 and CFC-12<sup>[9]</sup>. CAHs impede the biooxidation of methane<sup>[10]</sup> and significantly contribute to malodorous air and the greenhouse effect<sup>[9, 11]</sup>. Consequently, a critical research objective in carbon emission reduction is to thoroughly investigate the degradation mechanisms of CAHs in landfills and to develop effective control strategies.

The redox potential within a micro-aerobic environment is closely tied to oxygen concentration, with higher levels of oxygen leading to an increased redox potential<sup>[12]</sup>. Concurrently, fluctuations in oxygen concentration significantly affect the speciation and toxicity of pollutants. For instance, hexavalent chromium is considerably more toxic than trivalent chromium under conditions of elevated oxygen concentration<sup>[13]</sup>, while divalent manganese becomes more toxic at lower oxygen levels, markedly suppressing enzyme activities within biological cells. Research by Táncsics et al.[14] demonstrated that a micro-aerobic setting can stimulate the production of a novel toluene dioxygenase by Zoogloea, thereby facilitating the hydroxylation of toluene. A comparative analysis of methane (CH<sub>4</sub>) oxidation under micro-aerobic (2.5%) and aerobic (21%) conditions by Ruo He et al.<sup>[15]</sup> revealed that a micro-aerobic environment enhances the sequestration of CH<sub>4</sub> in soil as biochar and organic carbon, consequently reducing CO<sub>2</sub> emissions. Functional microorganisms within the environment exhibit altered metabolic activities in response to varying oxygen concentrations; some anaerobic microorganisms persist in anaerobic metabolism even under micro-aerobic conditions<sup>[16]</sup>, while aerobic microorganisms sustain high metabolic activity in such settings<sup>[17]</sup>. These findings underscore the necessity for further investigation into the role and impact of micro-aerobic environments in the context of environmental pollution remediation and microbial

processes.

The predominant clay composition of the landfill cover layer results in low oxygen transmission efficiency, leading to a predominantly micro-aerobic state within the cover<sup>[18]</sup>. This cover serves as a critical barrier against the release of landfill gases into the atmosphere, and over time, natural adaptation fosters the proliferation of numerous functional microorganisms<sup>[19]</sup>. The migration and transformation of landfill gases involve mechanisms such as convection, diffusion, adsorption, and biological degradation, with the latter two processes being especially pivotal for the removal of chlorinated hydrocarbons (CAHs)<sup>[11,20]</sup>. Understanding these migration and transformation dynamics is essential for effectively managing associated pollutants. Recent studies have concentrated on the biodegradation capabilities of mulch for HCFCs, encompassing laboratory-scale serum bottle experiments, simulated mulch conditions for HCFC degradation, and field-based pollutant degradation studies<sup>[21]</sup>. These studies indicate that the structural characteristics of chlorinated hydrocarbons play a significant role in their biodegradation, with the rate influenced by factors like temperature, initial concentration. material, coating and oxygen concentration, ranging 0.013 3.244 from to  $\mu g/(g_{soil} \cdot h)^{[22]}$ . The biodegradation of HCs in the coating is intricately linked to their adsorption properties, with both processes occurring concurrently and interacting within the coating. A precise evaluation of adsorption and degradation rates is vital for selecting an effective HCFC control strategy. While research has addressed the adsorption properties of chlorinated hydrocarbons in sediments and natural soils under both aerobic and anaerobic conditions, there is a gap in comprehensive and systematic research on the degradation characteristics of various chlorinated hydrocarbons in landfill gas within clayey soils under micro-aerobic conditions.

In this study, we systematically investigated the soil from an unclosed landfill in Chongqing. Initially, we acclimated the mulch soil to aerobic, micro-aerobic and anaerobic conditions. Subsequently, we conducted a biodegradation experiment on trans-1,2-dichloroethylene (t-1,2-DCE) under micro-aerobic conditions. Chlorinated aromatic hydrocarbons (CAHs) were detected using gas chromatography with an electron capture detector (GC-ECD), and a degradation equation for chlorinated olefins was formulated through kinetic analysis to assess t-1,2-DCE degradation within the soil matrix. The contribution of microbial oxidation in the mulched soil was evaluated based on mass balance considerations. Finally, employing the Illumina MiSeq platform, we performed high-throughput sequencing analysis on the t-1,2-DCE-degraded mulch. This analysis aimed to explore the alpha diversity of the soil microbial community and to elucidate the composition of microbial communities and functional strains within the mulch across varying oxygen concentration gradients. The overarching goal of this research was to offer theoretical insights to guide the degradation of chlorinated olefins in landfill covers across different cities, thereby aiding in carbon emission reduction efforts.

#### 2. Materials and methods

#### 2.1 landfill sampling

The cover soil samples of the simulated landfill used in this study were collected from Chongqing Rongchang Municipal Waste Treatment Plant (coordinates 29 23' 36.87 "N, 105 34' 24.41" E) which has operated for more than 12 years, and the daily waste treatment capacity of the plant reached 450 tons. Covering soil samples were collected from areas with a covering time of more than 2 years under the depth of 10 cm of the landfill cover, and larger particles such as stones and garbage were removed after collection, and then sieved, filtered and mixed evenly through a 2 mm soil sieve for subsequent use.

#### 2.2 Covering soil domestication experiment

The selected soil sample collection depth is set to be 0.1 to 0.3 m. Soil treatment consists of air-dried chipping, removal of stones and sieving through a 2 mm sieve. The water content of the treated soil sample was adjusted to 15%, and it was ready after 14 hours of balance. See the relevant literature for the physical and chemical properties of the covering soil<sup>[23]</sup>.

Aerobic/micro-aerobic acclimation: The mixed soil samples were subpackaged into 15 500 mL serum vials, with 250 g soil sample in each vial, and subjected to aerobic/micro-aerobic/anaerobic continuous acclimation using CH<sub>4</sub> as the substrate, respectively. Aerobic/micro-aerobic acclimation method: high-purity nitrogen was used to purge the air in the bottle for 2 min, the bottle was quickly sealed with a plug, and 100 mL CH<sub>4</sub> was used to replace the air in the bottle. Then 0.1-1 mg/L (concentration gradient: 0.1 mg/L) and 1-10.0 mg/L (concentration gradient: 2.5mg/L) oxygen were injected into the bottle with a syringe, and placed in a thermostatic incubator at 30 C. The above steps were repeated until the CH<sub>4</sub> concentration in the bottle was less than 2% or the O2 concentration was changed. The acclimation was continued for more than two weeks, and stopped when the CH<sub>4</sub> oxidation capacity was stable.

Anaerobic acclimation: high purity nitrogen was used to purge the air in the bottle for 2 min, and the bottle was quickly sealed with a plug. The gas in the bottle was replaced by 100 mLCH<sub>4</sub> and placed in a constant temperature incubator at 30 C. CH<sub>4</sub> in the bottle was continuously detected. When the CH<sub>4</sub> concentration in the bottle was less than 2%, the above steps were repeated. The acclimation was continued for more than two weeks, and stopped after the CH<sub>4</sub> oxidation ability was stable, for the degradation study of t-1,2-DCE<sup>[24]</sup>.

# 2.3 t-1,2-DCE Biological Degradation Experiment in micro-aerobic Environment

In the experiment, the constant temperature was kept at 30 C, pH was 6–7, and the water content of the soil sample was 15%. First, 50 g of covering soil sample was put into a 250 ml serum bottle, and landfill gas was used in a simulated aerobic/microaerobic/anaerobic environment. High-purity nitrogen was used to purge the air in the bottle for 2 min, and the bottle was quickly sealed to ensure sealing. Then, 50 mL CH<sub>4</sub> was used to replace the air in the bottle, and then  $O_2$  with different concentrations was injected into the bottle by a syringe to replace the air in the bottle.

Subsequently, approximately 2000 ppm of t-1,2-DCE was added to the vials using a 1 mL syringe and the serum vials were incubated at 30 C. A blank control group was established under the same conditions as the experimental group, except that the addition soil was sterilized soil. To ensure the repeatability of the experiment, three duplicate samples were prepared for each experimental group and the control group.

The serum vials were placed in a 30 C incubator and the initial concentrations of methane and t-1,2-DCE were recorded after 1 hour of stabilization. Their concentration changes were monitored periodically over the next 14 days. At the end of the experiment, the serum bottle was opened and 0.5 g of soil sample was taken for subsequent analysis. The soil samples before and after treatment were packaged in moisture-proof bags and stored at - 80 C for a series of experimental operations such as DNA extraction.

#### **2.4 Degradation Analysis and Detection**

t-1,2-DCE was detected by gas chromatography (ECD) (column: GDX; ; Nitrogen was used as the carrier gas). Chloride ion concentration was detected by ion chromatography (CED) (chromatographic condition: Dionex AG9-HC 2 mm protection column and Dionex AS9-HC 2 mm separation column). The halogenated hydrocarbon gas-liquid fraction was converted by Henry equation (Henry coefficient vs. temperature E=e(A-B/T)). The degradation products were detected by GC-MS (DB-5ms capillary column (30.0 m×0.25 mm)<sup>[25]</sup>.

#### 2.5 Dynamic analysis

The calculation of the apparent degradation rate and the net degradation rate of t-1,2-DCE are performed according to specific formulas, respectively<sup>[24]</sup>See Formula (1) and Formula (2) respectively.

$$v_{\overline{\mathcal{R}}} = \frac{C_{e} \cdot V_{e} - C'_{e} \cdot V'_{e}}{m_{e} \cdot t} \quad (1)$$

Where Ce was the initial concentration of t-1,2-DCE ( $\mu$ g L<sup>-1</sup>) in the experimental group, Ve was the gas phase volume (L) of the reaction system in the experimental group, Ce' was the concentration of t-1,2-DCE ( $\mu$ g L<sup>-1</sup>) after the reaction in the experimental group, Ve' was the gas phase volume (L) of the system after the reaction in the experimental group, me was the soil mass (g) in the experimental group, and T was the reaction time (h).

$$\mathbf{v}_{ij} = \frac{(\mathbf{C}_{e} \cdot \mathbf{V}_{e} - \mathbf{C}'_{e} \cdot \mathbf{V}'_{e}) - (\mathbf{C}_{b} \cdot \mathbf{V}_{b} - \mathbf{C}'_{b} \cdot \mathbf{V}'_{b})}{\mathbf{m}_{e} \cdot \mathbf{t}} \quad (2)$$

In the equation,  $C_b$  was the initial t-1,2-DCE concentration in the blank group ( $\mu g \cdot L^{-1}$ ),  $V_b$  was the gas phase volume of the reaction system in the blank group (L), CB ' was the concentration of t-1,2-DCE after reaction in the blank group ( $\mu g \cdot L^{-1}$ ), and VB ' was the gas phase volume of the system after reaction in the blank group (L).

#### 2.6 DNA extraction and microbial diversity

The overburden soil samples were stored at-80 C for biodiversity analysis. The total genomic DNA of the microorganisms was extracted from the samples using the mobiopower soil DNA isolation kit, and the DNA samples were purified by mobiopower clean DNA clean-up kit.

The quality of purified DNA was verified by 1% agarose gel electrophoresis. The V3+V4 highly variable region of the 16S rRNA of the microorganism was sequenced and analyzed. In order to ensure the quality of sequencing data, Trimmomatic and FLASH software were used to conduct strict processing on the original data, including eliminating low-quality bases and short segments, merging overlapping double-ended reading sequences, and screening out sequences that did not meet the conditions: (1) filtering the bases with the mass value less than 20 at the tail part of read, and setting a window of 50 bp; if the average value in the window is less than 20 bp, cutting off the back-end bases from the window, and filtering READ with the mass value less than 50 bp after quality control. (2) According to the overlap relationship between PE reads, the paired reads are merge into a sequence, and the minimum overlap length is 10 bp. (3) The maximum allowable mismatch ratio in the overlap region of the splicing sequence is 0.2, and the non-matching sequences are screened. (4) detect a box sequence at that tail end of the sequence, carrying out reverse complement on the sequence comprise the box at the initial end with a minimum mismatch number of 0, and removing the box. (5) barcode on the detection sequence is detected and samples are distinguished, and the barcode mismatch number is 0, and the maximum primer mismatch number is 2. All data processing and

analysis were performed using SPSS Statistics 21 and i-sanger platforms<sup>[25]</sup>.

#### 3. Results and Discussion

### 3.1 Degradation characteristics of t-1,2-DCE under micro-aerobic condition

Figure 1(a) depicts the degradation profile of t-1,2-DCE. Within the 0.1–0.5 mg/L range of oxygen concentration, rate escalated alongside the degradation the concentration gradient, with the 1,2-DCE concentration initially dropping and then stabilizing. At oxygen concentrations between 0.3-0.5 mg/L, the degradation rate peaked at 99%, surpassing all other groups. Figures 1(c) illustrate that 1(b) and under oxvgen concentrations of 0.6-1.0 mg/L and 2.5-10.0 mg/L, the degradation rates were relatively consistent at approximately 75%. These findings indicate that t-1,2-DCE is susceptible to co-metabolism and degradation by microorganisms across a concentration gradient under micro-aerobic conditions. The degradation efficacy initially improved with increasing oxygen levels but then declined, with optimal results observed at an oxygen concentration of 0.5 mg/L. This suggests that understanding the metabolic pathways of microorganisms involved in dichloroethylene degradation and how they are influenced by varying oxygen concentrations is essential for refining microbial degradation technologies, which can then be effectively applied to environmental remediation and waste management practices.



# 3.2 Analysis of contribution of micro-aerobic biological oxidation capacity in covered soil

Variations in oxygen concentration markedly influenced the degradation of chlorinated olefins, as illustrated in Figure 2. Anaerobically, the apparent degradation rates of t-1,2-DCE in sterilized and activated soils were 2 and 18  $\mu$ g·g<sup>-1</sup>·h<sup>-1</sup>, respectively. Under micro-aerobic conditions, the apparent degradation rate of t-1,2-DCE rose with increasing oxygen concentration, peaking at 29  $\mu$ g·g<sup>-1</sup>·h<sup>-1</sup> at 0.5 mg/L, beyond which it declined to approximately 19  $\mu$ g·g<sup>-1</sup>·h<sup>-1</sup> with further concentration increases. Aerobic conditions yielded an apparent degradation rate for t-1,2-DCE comparable to anaerobic conditions, suggesting that t-1,2-DCE degradation in covered soil is sensitive to oxygen concentration gradients, with degradation rates enhancing as concentrations rise.



Figure 2 Apparent degradation rate of t-1,2-DCE in a micro-aerobic environment

Figure 3 demonstrates that when t-1,2-DCE served as the substrate, the net degradation rate in an anaerobic environment was as high as 16  $\mu$ g·g<sup>-1</sup>·h<sup>-1</sup>. Notably, this rate peaked at 27  $\mu$ g·g<sup>-1</sup>·h<sup>-1</sup> under micro-aerobic conditions at oxygen concentrations of 0.4 and 0.5 mg/L. These findings underscore the substantial promotional effect of such an environment on the degradation process. It is plausible that at these oxygen levels, the presence of both aerobic and anaerobic bacteria, along with methane-oxidizing bacteria, capitalize on available oxygen to facilitate dechlorination, thereby enhancing the degradation



enhancement in t-1,2-DCE degradation rates within a micro-aerobic setting, further confirming the significant

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Figure 3 Net degradation rate of t-1,2-DCE in a micro-aerobic environment

### 3.3 Microecological response of t-1,2-DCE co-metabolism biodegradation process

Utilizing the high-throughput Illumina MiSeq sequencing technique, our analysis identified a total of 6,750 operational taxonomic units (OTUs) and yielded 1,002,549 valid sequence reads. The sequencing coverage across all 15 samples exceeded 98%, signifying that we have garnered a comprehensive understanding of the bacterial community structure present in the samples.

3.3.1 Analysis of significant differences in microbial diversity index at different concentrations: Alpha

diversity analysis of the microbial communities in degradable vinyl chloride mulch is presented in Table 2. The Ace index values were notably high, the Simpson index was consistently below 0.1, and the Shannon index exceeded 5.7, collectively indicating a rich diversity and abundance of microbial species. In the degraded cover soil, the sequencing coverage for the 15 samples was above 98.14%, accurately reflecting the diversity and structure of the bacterial communities present. Significant variations were observed under anaerobic, micro-aerobic, and aerobic conditions, particularly at oxygen concentrations ranging from 0.1 to 0.5 mg/L.

| Sample (mg/L)   | Ace        | Chao      | Coverage  | Shannon | Simpson | Sobs                |
|-----------------|------------|-----------|-----------|---------|---------|---------------------|
| anaerobic       | 3164.5079  | 3057.7851 | 0.9844    | 6.3713  | 0.0058  | 2683.0000           |
| 0.1             | 3129.2999  | 2980.6291 | 0.9845    | 5.7007  | 0.0311  | 2666.0000           |
| 0.2             | 3061.9920  | 2980.1795 | 0.9848    | 6.0927  | 0.0131  | 2600.0000           |
| 0.3             | 3204.3703  | 3153.6188 | 0.9826    | 6.1275  | 0.0130  | 2616.0000           |
| 0.4             | 2852.2150  | 2745.0090 | 0.9845    | 5.1084  | 0.0975  | 2317.0000           |
| 0.5             | 3030.5070  | 2978.9461 | 0.9852    | 6.1609  | 0.0158  | 2592.0000           |
| 0.6             | 3104.5017  | 3065.0100 | 0.9814    | 5.9552  | 0.0079  | 2378.0000           |
| 0.7             | 2652.8141  | 2594.7809 | 0.9866    | 6.0300  | 0.0075  | 2228.0000           |
| 0.8             | 2487.3538  | 2401.8324 | 0.9875    | 5.8734  | 0.0096  | 2089.0000           |
| 0.9             | 2892.8746  | 2828.2246 | 0.9845    | 5.9986  | 0.0093  | 2359.0000           |
| 1.0             | 3191.7856  | 3077.4791 | 0.9840    | 6.2113  | 0.0069  | 2711.0000           |
| 2.5             | 3166.9182  | 3100.4295 | 0.9842    | 6.4818  | 0.0039  | 2672.0000           |
| 5.0             | 3310.5821  | 3227.1747 | 0.9832    | 6.4629  | 0.0045  | 2792.0000           |
| 7.5             | 3479.1297  | 3345.0000 | 0.9817    | 6.4994  | 0.0049  | 2859.0000           |
| 10.0            | 3226.6888  | 3114.7125 | 0.9827    | 6.1604  | 0.0082  | 2643.0000           |
| 2.2.2. Comment' | f minutial |           | ( 1 2 DOE |         | 1       | <u>c</u> <u>t</u> 1 |

Table 1 Alpha diversity under micro-aerobic condition

3.3.2 Composition of microbial communities with different concentrations in mulch soil: The high-throughput sequencing analysis targeted microorganisms in the mulch soil under the stress of

t-1,2-DCE. Clustering analysis of operational taxonomic units (OTUs) under both aerobic and anaerobic conditions disclosed a classification of bacterial OTUs into 46 distinct phyla and 942 genera,

as detailed in Figure 6. At the phylum level, the microbial communities were dominated by Proteobacteria, Chloroflexi, Actinobacteria, Bacteroidetes, and Acidobacteria, which collectively constituted over 90% of the total. Notably, the Proteobacteria phylum was the most abundant, reaching nearly 45% relative abundance at an oxygen concentration of 1 mg/L. The microorganisms within the Proteus species are believed to contribute significantly to the degradation of t-1,2-DCE, primarily via co-metabolism. This suggests that these microbes may exert a predominant influence on the overall degradation mechanism of t-1,2-DCE.

As the oxygen concentration gradient decreased, we examined and analyzed the microbial community structure in the mulched soil following co-metabolic degradation within a micro-aerobic environment. Figure 4 presents the findings, with over 10 distinct across all samples, with a relative abundance of more than 30% at oxygen concentrations between 0.1-1 mg/L. included Other notably dominant phyla Gemmatimonadota, Acidobacteriota, and Chloroflexi. Notably, the Chloroflexi phylum was enriched under varying oxygen levels, suggesting that multiple dechlorination bacteria are classified under this phylum. High oxygen levels favored the enrichment of Chloroflexi in response to t-1,2-DCE, whereas under anaerobic conditions, t-1,2-DCE stimulated the enrichment of Patescibacteria. The dominant species involved in t-1,2-DCE degradation demonstrated significant variations under different oxygen concentrations, highlighting the sensitivity of the microbial community to oxygen levels.



Community barplot analysis

Proteobacteria emerged as the predominant phylum

Figure 4 Microbial community composition at the phylum level after t-1,2-DCE degradation in cover soil



Figure 5 Microbial community composition at the phylum level after t-1,2-DCE degradation in cover soil under micro-aerobic environment

To delve deeper into the correlation between shifts in biodiversity and the degradation of t-1,2-DCE throughout the enrichment and acclimation phases, we scrutinized the microbial community composition at the sub-class level under aerobic, anaerobic, and micro-aerobic conditions, with findings depicted in Figure 8. Under aerobic and anaerobic conditions, the predominant bacterial genera included norank-f-Gemmatimodaceae, MND1, and NORANK-F-VICINAMIBACTERACIAE.

Post-degradation, a novel Methlobater strain was detected, albeit at a low relative abundance, fluctuating between 0.31% and 2.08%. Furthermore, under anaerobic conditions during the co-metabolic degradation of t-1,2-DCE, the relative abundance of Sphingomonas, a key functional bacterial genus in the mulch soil, was observed to decrease to varying extents.

The analysis of the microbial community structure in

the degraded cover soil is presented in Figure 9. Notably, Methylomonas and Methylobacter, both significant methanotrophs within the cover layer, play a pivotal role in the removal of landfill gas. Their activity is crucial for the degradation of t-1,2-DCE through co-metabolism, with the micro-aerobic environment providing sufficient oxygen to support the growth of Methylomonas. Under anaerobic conditions and at oxygen concentrations of 0.5 mg/L and 1.0 mg/L, Methylomonas exhibited a considerably higher relative abundance at 0.5 mg/L, constituting 31.2% of the community. Moreover, the absolute abundance of dominant species, particularly methanotrophs, peaked at 0.5 mg/L, confirming that this oxygen level yielded the most effective degradation of t-1,2-DCE, followed closely by 0.4 mg/L. These findings suggest that the response of functional microorganisms in the mulch soil to chlorinated hydrocarbon stress varies with different oxygen concentrations. Methylomonas, being a micro-aerobic or facultative anaerobic microorganism,





occur in a micro-aerobic environment, particularly at an oxygen concentration of 0.5 mg/L.

Figure 6 Stacking bar chart of microbial community composition at genus level after t-1,2-DCE degradation in covering soil





3.3.3 functional strain in cover soil: Figures 8 and 9 present the results of the tests for significant differences between groups. Utilizing the community abundance data, we applied rigorous statistical methods to perform hypothesis testing on species within microbial communities across different groups or samples. This analysis aimed to evaluate the significance of species abundance differences and identify species with notable variations between groups or samples. In the comparative analysis of the total samples before and after t-1,2-DCE degradation, Methylomonas and Methylobacter exhibited significant advantages post-degradation. Specifically, at an oxygen concentration of 0.5 mg/L, the distinction between Methylomonas and Methylobacter became more pronounced, with methane primarily serving as the carbon source. These organisms are capable of metabolizing methane in both anoxic and oxygenated environments, facilitating the dechlorination and degradation of chlorinated aromatic hydrocarbons (CAHs) by the dechlorinating bacterial genus. The relative abundance of Sphingomonas remained non-significantly different before and after degradation;

methanotrophs. Beyond methane oxidation, certain strains of Methylobacter have demonstrated the capacity to degrade dissolved organic carbon compounds, suggesting their potential significance in environmental biodegradation and contaminant removal processes<sup>[26]</sup>.

differential analysis of microbial Additionally, community groups was performed using a ternary phase diagram, with the outcomes depicted in Figure 8. In this diagram, circles of the same color represent the same genus, and the area of each circle is proportional to the genus's abundance. Notably, Methylomonas, a key functional strain, exhibited a relative abundance of over 70% at an oxygen concentration of 0.5 mg/L, compared to approximately 30% in both anaerobic and aerobic conditions. This suggests that Methylomonas is better adapted to grow at an oxygen concentration of 0.5 mg/L. Consequently, variations in oxygen concentrations, along with the structural properties of chlorinated hydrocarbons and the extent of degradation, lead to differences in the adaptive capacity of the same strain. These factors are the primary drivers behind the



however, its activity was observed to be enhanced by observed differences in community structure.

Figure 8 Analysis of Ternary Phase Diagram after Domestication in hypoxic Environment



Figure 9 Test for significant differences between groups before and after treatment (a represents the significant difference between groups in all samples; b is the significant difference between groups when the oxygen concentration is 0.5 (mg/L)

#### 4. Conclusion

The primary objective of this study was to elucidate the biodegradation characteristics of (t-1,2-DCE) under micro-aerobic conditions within landfill covers. Our findings indicate that t-1,2-DCE is susceptible to microbial degradation across a concentration gradient under micro-aerobic conditions, with degradation efficiency escalating as oxygen concentrations increase from 0.1 to 0.5 mg/L. Notably, at an oxygen concentration of 0.5 mg/L, the degradation rate soared to 99%, marking the peak performance. The highest net degradation rate recorded was 27  $\mu g \cdot g^{-1} \cdot h^{-1}$  at oxygen concentrations of 0.4 and 0.5 mg/L. The micro-aerobic environment was found to supply ample oxygen for the proliferation of Methylomonas, a key methanotroph in the cover layer, which exhibited robust methane activity. Both oxidation Methylomonas and Methylobacter demonstrated significant advantages in degrading t-1,2-DCE, predominantly utilizing methane as their carbon source. The study further confirmed that aerobic and anaerobic co-metabolism can concurrently occur in a micro-aerobic environment, particularly at an oxygen concentration of 0.5 mg/L. Consequently, methanotrophs are pivotal in facilitating the co-metabolic degradation of t-1,2-DCE. This research has enhanced our comprehension of the biodegradation of chlorinated olefins under micro-aerobic conditions and offers strategic insights for the mitigation of methane emissions in conjunction with the degradation of typical chlorinated olefins. Future investigations should explore the mechanisms underlying the biodegradation of chlorinated olefins. Furthermore, while this study was specific to a landfill in Chongqing, the broader applicability of these findings to landfills in other regions warrants further exploration, suggesting the need for expanded research across various geographical locales.

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## EXPLORING THE POTENTIAL OF SATELLITE DATA FOR LANDFILL AND DUMPSITE MONITORING IN AFRICA – ANNOTATION BY SAM

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#### ABSTRACT

Landfills and dumpsites remain a significant aspect of waste management in the developing world and Africa is not an exception. With little to no management of these sites, there is a dearth of knowledge about the contribution of the African continent to the global waste and environmental issues. Due to the informal nature of some of these sites and limited management, their location is not always well documented. The use of satellite images for identification of landfill sites is therefore an appropriate option for the case of Africa. This study uses the Segment Anything Model (SAM) to annotate landfill and dumpsites in Africa. Annotation is one of the first and crucial steps of image analysis and must be as accurate as possible. The study used 54 satellite images from different countries in Africa and was able to obtain an average annotation accuracy of 96.21% for the landfill and dumpsites. Furthermore, the study determined that the annotation accuracy of SAM is influenced by the scale factor or zoom level of the image.

Key Words: landfill, dumpsite, annotation, satellite imagery, remote sensing, SAM

#### INTRODUCTION

The United Nations (UN) predicts that the African population (1.3billion) is expected to double in next 50 years [1]. More than 90% of African countries use landfills and or dumpsites as the only viable option for waste disposal. It therefore follows that the increased amount of waste driven by this rapid population growth will add to an already burdened waste sector. According to [2], landfills in large municipalities across South Africa are nearing full capacity way before their planned lifespan. One of the major challenges of the waste sector in Africa is poor management of landfills as well as the emergence of informal dumpsites. In the absence of waste minimisation, recovery, recycling, or reuse initiatives in developing countries, waste is often either incinerated or disposed of in poorly designed landfills or simply in nearby lagoons, rivers, lakes, or designated spots on the streets. This poses severe social, economic, and environmental threats to urban residents [3]. An international team commissioned by the United Nations (UN) highlighted the urgent need for improved

availability and reliability of waste and resource data [1]. Landfills and dumpsite tracking, and management represent critical areas requiring improvement, particularly in developing countries. Traditional methods such as field surveys are time consuming and labour-intensive, posing challenges for large-scale landfill detection [4]. Technological advancements such as remote sensing (RS) and Geographic Information Systems (GIS) are gradually being utilised in the management of large landfills [5]. While visual interpretation remains a basic method for landfill identification, recent years have seen the emergence of mathematical and statistical techniques for improved detection in remotely sensed images. For example, [6] utilised remote sensing to identify potential illegal waste landfills in Andalusia and applied logistic regression to predict landfill occurrences. Similarly, [7] remote employed sensing interpretation and discriminant analysis to map potential illegal landfills in Gran Canaria and La Palma. However, many existing studies have produced probability maps of landfill distributions without precise identification [4]. То

address this gap, machine learning models offer promising solutions. [8] compared algorithms for illegal dump detection in Russia, highlighting neural network classification as the most accurate and efficient. [9] proposed a support vector machine (SVM) approach for waste dump detection in Uganda using Sentinel data. Meanwhile, [10] analysed features of construction and demolition waste (CDW) landfills, developing an optimal method combining morphological indexing and hierarchical segmentation for identification. However, traditional machine learning methods often rely on manually selected features and fall short in achieving automatic landfill identification. Segmentation is an essential step for remote sensing image processing. Segmentation allows us to isolate specific objects or areas within an image for further study or monitoring [11]. By combining machine learning algorithms with image processing and computer vision techniques, waste may be automatically identified and categorised based on visual characteristics [12]. The Segment Anything Model (SAM), engineered by Meta AI, represents a pioneering method in image segmentation, showcasing remarkable generalisation capabilities across various image datasets, without the need for additional training for unfamiliar objects [13]. This unique approach empowers SAM to deliver precise predictions even when faced with limited or absent training data. Moreover, this zero-shot learning, makes it a promising approach to processing aerial and orbital images from diverse geographical contexts [14]. Another significant aspect concerns SAM's capacity to conduct segmentation with minimal input, necessitating solely a bounding box, a single point as a reference, or even a prompt text as guidance [13]. This functionality holds promise for reducing human effort during the annotation process. Numerous current methods demand extensive annotations for every new object of interest, leading to substantial computational burdens and potential delays in time-sensitive scenarios [14]. Conversely, SAM offers a chance to alleviate this time-consuming task. To the best of our knowledge, SAM has not been explored for the application of landfill site detection. This study therefore aims to explore the efficacy of SAM in identification of landfill sites by way of annotation. The boundary box prompt was selected as the investigatory point due to its ability to select a large area of interest in an image as is the case with landfill sites.

## METHODOLOGY

## **Data collection**

To obtain landfill and dumpsites in Africa, a desktop search was carried out. Firstly, names of African countries were searched and listed out. Then beginning from south to north searches of "landfill" and "dumpsite" in each country were carried out on Google Search as well as Bing Search. The names of the sites were listed down with the aim of obtaining at least three (3) names per country. These names were obtained from different sources such as academic papers, news blogs and social media. Where possible, the location of the site was recorded but for majority of the sites there was no indicated location or address. The names and or addresses of the sites where then searched for on Google Maps and a visual inspection was carried out. This visual inspection resulted in a list of fifty-four (54) sites across different countries. A summary of the process is outlined in figure 1.



Figure 1. Process flow of data collection

#### **Dataset creation**

Once the raw data was compiled, the study proceeded to create the dataset. For this dataset creation, ESRI World Imagery with only Red: Green: Blue (R:G:B) band was used to obtain remote sensing images of the landfill sites. Images were selected from a period between January 2021 and January 2024 based on the clarity and periods without cloud cover. Furthermore, to ensure that a complete landfill site was captured with high spatial resolution, a size of 1280 x 1280 pixels was chosen for each image download. The images were downloaded from ArcGIS Pro in TIFF file format and arbitrarily named Map\_1 to Map\_54 for ease of handling. Since it was not known which aspect ratio was ideal, three batches were downloaded with different scale factor/zoom level and conveniently named Near, Middle, Far. These were based on the clarity of the image in relation to the scale factor with Near being the nearest possible image where all of the landfill/dump site can be visualised clearly and Far being the furthest that can be visualised clearly as shown in figure 2.



Figure 2. Landfill images showing Near, Middle, and far scale factor/zoom level.

#### Annotation

Following the downloading of images, manual masks were created for comparison with the SAM. To ensure that both sets of annotations (manual and SAM) are comparable, DigitalSreeni Image Annotator was used. DigitalSreeni Image Annotator is a robust and user-friendly tool for annotating images with polygons and rectangles, developed using PyQt5 [15]. It allows for both manual annotation and SAM-assisted annotation. Landfill/dump site label was created, and the manual annotation was done by drawing polygons around the sites and saving the annotations in JSON and PNG file formats as well as YOLOv8. For annotation with SAM, the SAM2 small model was selected. The application uses a bounding box (rectangle) for selection of area of interest and provides various outputs with different scores and only the top-scoring region will be displayed [15].

#### **RESULTS & DISCUSSION**

#### **SAM scores**

When using the SAM for annotation, various output with different scores are displayed. These scores are displayed in decimals of less than 1. It was observed that the output scores do not necessarily indicate the accuracy of the model as some of the high scoring outputs were not much smaller than the site as shown in figure 3.



Figure 3. Comparison of different SAM output scores (0.78, 0.87, 0.74, 0.81) to dump site Image and manually annotated mask (Mask Au)

From figure 3, it is observed that the SAM annotation which has an outcome score of 0.87 (SAM\_0.87) covers a lesser area of the dumpsite as compared to those with outcomes of 0.78 (SAM\_0.78) and 0.81 (SAM\_0.81). Furthermore, there was weak correlation between the outcome scores and the accuracy of the SAM annotations, with a Pearson Correlation

Coefficient (r) of 0.38. This seemed unusual at first, but further investigation revealed that these output scores are probabilities [16]. Consequently, accepting the top result is not always ideal and therefore may require multiple inputs before achieving the required accuracy.

#### SAM accuracy

Manually generated annotations were used to compare the accuracy of the SAM annotations. Both the manual and SAM annotations were converted to binary form with each annotated image (mask) having pixel values of zero (0) and one (1) only. The accuracy is then calculated as the ratio of matching pixels (True Positives + True Negatives) between the two, to the total number of pixels, multiplied by 100 to express it as a percentage.

$$Accuracy = \frac{(True \ Positives + True \ Negatives)}{Total \ Pixels} * 100$$

The average accuracy of the three batches of images (Near, Middle, Far) are shown in figure 4.



Figure 4. The distribution and average accuracy percentage across the three zoom levels (Near, Middle, Far)

From fig.4, it is observed that the average accuracy for Near is 86.57%, Middle is 90.24% and Far is 96.21%. The results show that the Far zoom level, which is the furthest point at which the landfill or dump site can be visually identified yielded the highest annotation by SAM. Conversely, the Near zoom level yielded the lowest accuracy level. This result is intriguing as the closer the zoom level, the better the clarity of the image and expectation would be that the accuracy would increase. The possible explanation could be that since landfill and dump sites do not have a uniform pixel value, trying to segment them from at pixel level is difficult. However, when zooming out, the model can identify the boundary of the site in addition to the pixels. Moreover, when zooming out, the pixel values of the site are grouped making it easier for the model to identify.

### CONCLUSION

This paper represents an initial step in the advancement of landfill monitoring in Africa. The challenges involve misclassification of landfills and dumpsites as well as inaccurate identification of regions in landfill monitoring. The paper proposes the use of SAM for annotation of landfill and dump sites as a quick and reliable method. The SAM is compared to manual annotation, and it is found that it achieves high accuracy particularly when adjusted scale factor. This method can therefore be applied to develop a landfill dataset in Africa which can be used in other applications. Limitation of this method is that it requires the user to possess knowledge of landfill and dump sites to be able annotate as it is not fully automated. Moreover, it would be beneficial to investigate the relationship between the size of the bounding box of SAM and accuracy of detection. The next step is to use multispectral and hyperspectral images as well as other deep-learning methods to further advance landfill monitoring in Africa. These images will be best suited when exploiting the unique characteristics of such landfill and dumpsites, for instance the presence of plastics, increased surface temperature and even landfill gases.

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## **Estimation of Plastic Fishing Gear Marine Leakage from Fishing Vessel Fisheries in Japan**

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### Abstract

Marine plastics are recognized as an important issue that urgently needs to be resolved. A survey of drifted litter conducted by the Ministry of the Environment at 10 beaches across Japan reported that approximately 70% of the litter that drifted ashore by weight was plastic products, including fishing gear, and that litter from the fishing industry accounted for approximately 30% of the total. Therefore, this study aimed to estimate the national marine discharge of plastic fishing gear used for fishing boats and used at sea and in the sea. Specifically, the amount of plastic fishing gear discharged into the ocean per ton of catch using three survey methods ((1) a survey in which fishermen were asked to record fishing gear discharges during operations, (2) a survey combining fishing gear purchase records of fishermen and a questionnaire on the rate of fishing gear discharges into the ocean, and (3) an interview survey with fishermen) was estimated and multiplied by the national catch by fishing method. Nine fishery types were surveyed: purse seine, set net, trawl net, gill net, scoop net, basket net, longline fishing, squid fishing, and towline fishing. The results showed that an estimated 2,507 tons of plastic fishing gear was estimated to be discharged into the ocean from Japan's fishing vessels in one year. Characteristics of fishing methods that are more likely to result in gear being spilled include fishing methods that use fishing lines and fishing methods in which the gear is independent of fishing vessels and people.

## 1. INTRODUCTION

Marine plastics are recognized as a critical environmental issue that demands urgent resolution. According to a survey on coastal debris conducted at ten locations across Japan by the Ministry of the Environment, approximately 70% of beach litter by weight comprises plastic products, including fishing gear, with around 30% originating from the fishing industry. However, there have been limited quantitative studies on the loss volume of plastic fishing gear from fisheries.

This study aims to estimate Japan's national volume of plastic fishing gear leakage into the ocean from fishing vessel fisheries, particularly focusing on plastic fishing gear used on the water surface or in the sea. We conducted an investigation on nine types of fisheries, including purse seine, set net, trawl, gill net, scoop net, pot trap, longline, drifting barrel, and trolling in the Kyushu and Hokkaido regions, estimating the loss volume per unit catch of plastic fishing gear and the loss rate into the ocean.

## 2. ESTIMATION OF PLASTIC FISHING GEAR LEAKAGE

## 2-1 Methodologies

To estimate the marine leakage of plastic fishing gear, this study employed three research methods: (1) operational records, (2) purchasing records and survey on loss rates, and (3) interviews with fishermen. We calculated the unit loss by dividing the estimated loss of plastic fishing gear during the survey period by the fishing activity volume. Some fishing gear, such as nets and artificial lures, contain non-plastic materials like lead and aluminum, but this study focuses on plastic fishing gear, which may include non-plastic materials as well.

## (1) Estimation based on operational records

This survey targeted longline fishing, squid fishing (floating fishing), and trolling. Fishermen were asked to record details in their operation logs over a three-month period if any plastic fishing gear was lost during their activities. The log items included the type and quantity of fishing gear used on that day, the type and quantity of gear lost, among other details, enabling an estimate of the amount of loss as described later. To convert the recorded quantity of lost gear into weight, standard fishing gear actually used in each fishing method was provided, and weights were measured by gear type. The marine plastic fishing gear loss  $D_1$  (kg) during the survey period was estimated using Equation (1), by multiplying the unit weight  $w_{1,i}$ (kg/item or kg/m) of each type of plastic fishing gear *i* by the quantity or length  $n_{1,i}$  (items or meters) of gear lost during the target period.

$$D_1 = \sum_i w_{1,i} \cdot n_{1,i} \cdots \quad (1)$$

(2) Estimation based on purchasing records and loss rate surveys

This survey focused on squid fishing (floating fishing) and longline fishing. Data on the quantity and length of plastic fishing gear were extracted from purchase records of fishing gear during the fishing season from standard squid fishing and longline fishing operations. The weight of the purchased plastic fishing gear was estimated through interviews with fishing gear manufacturers and actual measurements. Additionally, to investigate the percentage of gear purchased to replace fishing gear lost to the sea during operations, a questionnaire was conducted with 12 squid fishing (floating fishing) fishermen and 31 longline fishermen. The marine plastic fishing gear loss  $D_2$ was estimated using Equation (2), by multiplying the estimated weight  $w_{2,i}$  (kg) of each plastic fishing gear type from purchase records by the percentage  $p_{2,i}(-)$  of purchased gear intended to replace lost gear, as indicated in the survey responses.

$$D_2 = \sum_i w_{2,i} p_{2,i} \cdots (2)$$

(3) Estimation based on interviews with fishermen

This survey targeted medium-scale purse seine fishing, large-scale stationary net fishing, salmon stationary net fishing, gillnet fishing, small-scale bottom trawl fishing, dip net fishing, and basket net fishing operations. The interviews covered aspects related to activity volume, such as the number of operating days and catch volume, as well as details about the fishing method, the types, specifications, quantities, sizes (lengths) of plastic fishing gear that may be lost to the sea, the frequency of losses, and the causes of these losses. For fishing methods that reported minimal gear loss, it was assumed that one set of gear would be lost once every 30 years. To convert the information obtained from the interviews into weight, inquiries were made to fishing gear manufacturers, and actual measurements were conducted. The marine plastic fishing gear loss  $D_3$  (kg) was estimated using Equation (3), by dividing the weight  $m_{3,i}$  (kg) of each type of plastic fishing gear *i* by the average period  $f_{3,i}$ (years) between incidents of gear loss for that type.

$$D_3 = \sum_i m_{3,i} / f_{3,i} \cdots (3)$$

#### 2-2. Estimation of plastic fishing gear loss

First, based on the information on plastic fishing gear used per day of operation obtained from the operational record survey and interview survey, the weight was calculated using the same method as for estimating basic units. The weight of plastic fishing gear used per day of operation was determined by multiplying the weight of plastic gear per set by the number of sets used in a single day. The estimated marine plastic gear loss rate was then calculated by dividing the weight of plastic gear lost per day per fishing operation by the daily usage.

Table 1 shows the survey methods, locations, primary target fish species, operating months or days, recent catch volumes, vessel sizes, and numbers based on interview results for nine types of fishing included in this study. Table 2 displays the main types of fishing gear prone to loss, the reasons behind the loss, and the frequency of occurrences. For net-based fishing methods such as purse seine, stationary net, bottom trawl, gillnet, dip net, and basket net fishing, nets were identified as the main type of gear lost. The main causes were damage to nets from getting caught on reefs and natural events, such as rough seas, leading to gear loss. In contrast, for fishing methods using lines, such as longline, squid fishing, and trolling, lures and lines were the primary gear lost, often due to larger fish biting through the line. The frequency of gear loss was higher for line-based fishing compared to net-based fishing.

The estimated marine plastic gear loss rate per basic unit for the nine types of fishing surveyed is

| No.   | Fishery type                             | survey method                       | research location      | Survey<br>Period         | Main species of fish to be caught   | Months or days of operation        | haul (catch)<br>of fish |
|-------|--|-------------------------------------|------------------------|--------------------------|---|------------------------------------|-------------------------|
| 1     | Purse seine<br>fishing                   | purchasing<br>records<br>interviews | Munakata,<br>Fukuoka   | October<br>2021          | Yellowtail, Mackerel, Horse Mackerel, Blue Mackerel, Round<br>Mackerel          | 9 months (April-December)          | 420t                    |
| 2     | 2 Octoret fictions into it               |                                     | Tsushima,<br>Nagasaki  | December<br>2022         | Yellowtail, Yellowtail Kingfish, Tuna, Grunt, Squid                             | 300 days (12 months)               | 180t                    |
| 3     | Set-net lishing                          | Interviews                          | Tomakomai,<br>Hokkaido | January<br>2024          | Salmon, Mackerel  | 45 days (September to<br>November) | 300t                    |
| 4     |  |                                     | Hakata,<br>Fukuoka     | November<br>2022         | Octopus, Silver Biddy, Flounder, Sea Bass, Shrimp                               | 100 days (April-December)          | 15 t                    |
| 5     |  |                                     | Tomakomai,<br>Hokkaido | January<br>2024          | Scallop, Flounder   | 40 days (December to March)        | 32t                     |
| 6     | Bottom trawl<br>fishing                  | interviews                          | Tomakomai,<br>Hokkaido | January<br>2024          | Surf Clam   | 90 days (December - April)         | 11t                     |
| 7     |  | -                                   | Mukawa,<br>Hokkaido    | January<br>2024          | Surf Clam, Trough Shell, Sakhalin Surf Clam                                     | ten days                           | 5.0t                    |
| 8     |  |                                     | Mukawa,<br>Hokkaido    | January<br>2024          | Shishamo, Ryukyu Fish, Saffron Cod  | 21 days (October-November)         | 75 t                    |
| 9     | Gillnot fishing                          | interviewe                          | Tomakomai,<br>Hokkaido | January<br>2024          | Alaska Pollock, Atka Mackerel, Sailfin Poacher, Flathead Flounder               | 100 days (October - February)      | 65t                     |
| 10    | Ginnet fishing                           | Ton<br>Ho                           | Tomakomai,<br>Hokkaido | January<br>2024          | Flounder, Skates, Shark, Cod, Raven Fish  | 38 days (May-July)                 | 8.4t                    |
| 11    | Dip net fishing                          | interviews                          | Tsushima,<br>Nagasaki  | December<br>2022         | Black Scraper   | thirty days                        | 4.8t                    |
| 12    | Basket trap fishing<br>(crabs, lobsters) | interviews                          | Tomakomai,<br>Hokkaido | January<br>2024          | Whelk, Spiral Shell   | 110 days (March-October)           | 11t                     |
|       |  | purchasing<br>records               | Munakata               | October<br>2021          | Tiger Puffer, Spanish Mackerel, Blackspotted Puffer, Raven<br>Fish              | 3 months (January - March)         |                         |
| 13 Lo | Longline fishing outflow                 | outflow records<br>interviews       | Fukuoka                | 2023<br>February<br>2023 |   | twenty-first day of the<br>month   | 1.8t                    |
|       |  | purchasing<br>records               | Munakata               | October<br>2021          | Sucretin Souid Securick Machanel Vallaustail Vallaus Crauman                    | 12 months                          | 2.9t                    |
| 14    | Floating fishing                         | outflow records<br>interviews       | Fukuoka                | 2023<br>February<br>2023 | Sworoup Squid, Spanish Mackerel, Tellowtall, Tellow Grouper,<br>Yellow Seabream | (10 days)                          | (0.35t)                 |
| 15    | Trolling fishing                         | outflow records                     | Munakata,<br>Fukuoka   | 2023                     | Spanish Mackerel, Yellowtail  | (15days)                           | (0.27t)                 |

Table 1 Details on the fishing gear loss survey

presented in Table 2. The table shows the marine plastic gear loss rate per fishing operation per day and per ton of catch. For fishing types surveyed across multiple operations (stationary net fishing, bottom trawl, and gillnet fishing), the total marine plastic gear loss, catch volume, and activity volume (such as operational days) were summed and then divided by the number of operations surveyed to calculate the average rate.

In terms of marine plastic gear loss per ton of catch, line-based fishing showed a higher loss rate than net-based fishing. Within net-based fishing, gillnet, basket net, and stationary net fishing had relatively high rates. Fishing methods with loss rates exceeding 0.1 kg/t, excluding trolling, shared the common characteristic of gear not being connected to the vessel. These findings led to the categorization of four groups, as illustrated in Figure 1, based on the tendency for gear loss.

The estimated marine plastic gear loss rate per fishing operation per day for the nine types of fishing surveyed is shown in Table 3, which includes the daily plastic gear usage and marine loss rate per fishing operation. For fishing types surveyed across multiple operations (stationary net, bottom trawl, and gillnet fishing), the average values across operations were used.

| Lable / Plactic tiching gear loce ner baci    |         |
|---|---------|
|   | • 11m1f |
| 1 abiez. 1 lastie fishing gear loss per basic | / umi   |

| Fishery type         | Plastic outflow per<br>management entity<br>per operating day<br>(kg-plastic gear<br>loss/operating days) | Plastic outflow per 1<br>ton of catch<br>(kg - plastic gear<br>loss/t - catch) |
|----------------------|---|--|
| Purse seine fishing  | 0.16  | 0.073  |
| Fixed-net fishing    | 0.19  | 0.14   |
| Bottom trawl fishing | 0.053   | 0.099  |
| Gillnet fishing      | 0.57  | 1.1  |
| Dip net fishing      | 0.0062  | 0.038  |
| Basket trap fishing  | 0.066   | 0.66   |
| Longline fishing     | 1.5   | 14   |
| Floating fishing     | 0.036   | 1.4  |
| Trolling fishing     | 0.0057  | 0.24   |

Table3. Plastic fishing gear loss rate

| Fishery type         | Plastic fishing gear<br>use per operating day<br>(kg-plastic gear use<br>/operating days) | Plastic loss rate per<br>management entity<br>per operating day<br>(%) |
|----------------------|---|--|
| Set-net fishing      | 5,937   | 0.0019   |
| Bottom trawl fishing | 100   | 0.067  |
| Gillnet fishing      | 1,388   | 0.058  |
| Dip net fishing      | 1,772   | 0.00035  |
| Basket trap fishing  | 416   | 0.016  |
| Longline fishing     | 39  | 3.8  |
| Floating fishing     | 7   | 0.48   |
| Trolling fishing     | 3   | 0.19   |



Fig 1 Grouping of fishing methods based on the likelihood of gear loss

The national marine plastic gear loss volume in Japan was estimated by multiplying the estimated unit rate per ton of catch by the national catch volume for each fishing type. For fishing types not included in the survey, four groups (from Figure 1) were used, applying the average unit rate for each group.

The estimated national marine plastic gear loss volume was approximately 2,507 tons (Table 5). By fishing type, gillnet fishing (144 tons) accounted for the highest loss in net-based fishing, while longline fishing (1,674 tons) had the highest loss in line-based fishing.

| Fishery type                | Amount of fish<br>catch<br>(1,000t) | Amount of plastic fishing gear loss (t) |
|-----------------------------|-------------------------------------|---|
| Bottom trawl fishing        | 673                                 | 67                                      |
| Seine net fishing           | 156                                 | 11                                      |
| Purse seine fishing         | 1,317                               | 96                                      |
| Gillnet fishing             | 134                                 | 144                                     |
| Set-net fishing             | 19                                  | 1                                       |
| Fixed-net fishing           | 436                                 | 61                                      |
| Other net fishing           | 38                                  | 13                                      |
| Longline fishing            | 122                                 | 1,674                                   |
| Pole-and-line fishing       | 97                                  | 23                                      |
| Squid fishing               | 29                                  | 42                                      |
| Trolling fishing            | 11                                  | 3                                       |
| Other types of line fishing | 23                                  | 88                                      |
| Other method of fishing     | 133                                 | 282                                     |
| Total                       | 3,189                               | 2,507                                   |

Table4. Amount of plastic fishing gear loss

# 2-3 Efforts by fishermen and fisheries cooperatives to address plastic gear loss

During interviews, all fishermen emphasized that gear loss was unintentional, and they made their best efforts to prevent it. Particularly with fishing nets, considerable attention was given to avoid damage or loss due to the high replacement cost. Additionally, some municipalities and fisheries cooperatives implemented programs for collecting and reusing fishing nets and ropes. This initiative is considered effective in preventing gear from being abandoned along shorelines and serves as a countermeasure against marine plastic gear loss, contributing to resource recycling.

## 3. CONCLUSION

The results obtained from this study are summarized as follows:

- The estimated amount of plastic fishing gear lost to the ocean from vessel-based fisheries was 2,507 tons.
- Line-based fishing methods may have a higher probability of plastic fishing gear loss to the ocean compared to net-based fishing.
- Fishing methods where gear is not connected to the fishing vessel have a greater likelihood of plastic fishing gear loss.

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## DEVELOPMENT OF LOW-CEMENT MARINE MATERIALS USING COMBINED COAL FLY ASH, MUNICIPAL INCINERATION FLY ASH, DESULFURIZED GYPSUM, AND ORDINARY PORTLAND CEMENT

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### INTRODUCTION

Several sectors, particularly building and waste Management, seek to use sustainable development strategies. The most common building material used worldwide is cement; however, its mass consumption is indirectly harmful to the environment, accelerated by the growing global demand; the cement production industry accounts for around 8% of global carbon dioxide emissions (Belaïd, 2022) (Andrew, 2019). Consequently, there has been an increased emphasis on reducing the use of cement and producing alternative materials for concrete manufacture (Santos et al., 2023), which has led to the research of industrial waste materials like fly ash, slag and silica fume. Municipal solid waste incineration fly ash (MSWIFA) and pulverized coal fly ash (PCFA) offer significant potential as supplementary cementitious materials (SCMs), especially in the development of low-cement marine concrete gels designed to endure aggressive marine environments (Xu et al., 2024), (Tozlu et al., 2021). Over the years, there has been a documented increase in the discharge of MSWIFA due to advancements in incineration technology and an increase in waste, which has resulted in an average yearly discharge of at least 10 million tons of MSWIFA from China (P. Wang et al., 2019). MSWIFA contains heavy metals and dangerous organic compounds, including dioxins, which can harm human health and the environment and are classified as hazardous waste (Wei, Li, and Liu, 2022). Before disposing of MSWIFA in landfills, it is treated to meet the conditions of national standards set out in GB 168892008, which applies to landfills to control pollution. The solid waste-extraction procedure for leaching toxicity using an acetic acid buffer solution method (HJ/T 300-2007) is standard in China. It assesses the leachability of heavy metals from solid waste and resembles the toxicity characteristic leaching procedure (TCLP) used elsewhere. This method uses acetic acid at a pH of 2.64 as the leaching solvent, simulating conditions that solid waste might encounter in a mixed municipal solid waste (MSW) landfill scenario (Duan et al., 2024). According to research, the most effective method for treating heavy metals in fly ash is immobilisation in cementitious materials (Guo et al., 2017), (Giergiczny & Król, 2008), (Tang et al., 2020). In our experiment,

we will test the leaching of heavy metals in marine environments using a similar procedure. Compressive strength and the ability to retain heavy metals when OPC is supplemented with different ratios of SCMs in a seawater environment were examined. Studies have demonstrated that MSWIFA and PCFA can produce concrete gels with lower cement content while maintaining or improving key properties, such as compressive strength, water absorption, and chloride resistance (Saxena and Baghban, 2023). The impact resistance of concrete containing 30% FA was greater than that of ordinary concrete (Navak et al., 2022a). This synergistic use of MSWIFA and PCFA reduces the carbon footprint associated with cement production and diverts significant amounts of industrial by-products from landfills, contributing to circular economy goals. Following the standard GB/T 38140-2019, it is used to simulate the corrosive properties of seawater. Under such conditions, the leaching of heavy metals in the low-cement marine concrete will be tested using the standard HJ 557-2010. Combining ordinary Portland cement (OPC) with SCMs such as MSWIFA and PCA to develop low-cement marine concrete gels focuses on enhancing the sustainability of concrete production by reducing cement usage, which is essential for lowering carbon emissions associated with traditional concrete manufacturing (Xu et al., 2024). By optimising the mix design of OPC and SCMs, a balance of the best performance and environmental impact will be evaluated.

The fly ash utilized in this experiment was analyzed and found to have a high calcium and chlorine content, with other minor elements like potassium, sodium and silicates. Incorporating fly ash into concrete will form additional cementitious compounds during hydration, leading to a denser microstructure that enhances longterm performance (Xinghua et al., 2016) . PCFA, commonly known as fly ash, plays a crucial role as an SCM in concrete due to its pozzolanic properties (Nayak et al., 2022b) . PCFA reacts with Ca (OH)<sub>2</sub> (produced during the hydration of Portland cement) in the presence of water, forming additional calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H). This reaction enhances the strength and durability of concrete over time

Concrete in marine environments faces unique challenges (Islam et al., 2012) due to the aggressive

saline conditions, which accelerate degradation mechanisms such as chloride ion penetration, sulfate attack, and corrosion of embedded steel reinforcement (Saxena & Baghban, 2023). The concrete structure in the tidal zone undergoes dry-wet cycles due to tidal motions and erosion by chloride ions (Cl<sup>-</sup>) in seawater and CO<sub>2</sub> in the air. The combination of these components might cause considerable damage to marine concrete construction.

Chlorine corrosion in marine concrete contributes significantly to structural failures, mainly because of the presence of chloride ions (Lim et al., 2021) primarily due to salts available in seawater, which can lead to the formation of harmful compounds in concrete in marine environment (Chang et al., 2021), such as a product compound calcium chloroaluminate in other words, Friedel's salt and calcium chloride. The mechanism of chloride attack on concrete can be summarised in the following chemical reaction, where sodium chloride (NaCl) and magnesium chloride (MgCl) combine with calcium hydroxide Ca(OH)2 to generate calcium chloride (IOP Conference Series: Earth and Environmental Science Utilization of Sea Water to Production of Concrete in Terms of Mechanical Behavior, n.d.).

 $Ca (OH)_2 + 2NaCl \longrightarrow CaCl_2 + 2NaOH \dots (1)$   $CaCl+3CaO \cdot Al_2O_3 + 10H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2$  $\cdot 10H_2O \dots (2)$ 

These chemicals interact negatively with the hydrating products of cement during curing. When chlorides permeate the concrete, they react with cement hydration products, which may alter the microstructure. Calcium chloride formation can exacerbate corrosion by attracting moisture and increasing concrete permeability (Effects of Salt Water on Concrete - PDF Material, n.d.) . Calcium chloride generation can accelerate corrosion by drawing moisture and increasing concrete permeability. The interaction between chlorides and cement pastes increases corrosion and influences the overall durability of concrete structures. (Chen & Ye, 2023). Chlorides can cause increased permeability, allowing more aggressive chemicals to permeate, as well as changed hydration kinetics, which can damage the concrete matrix over time (Barberon et al., 2005)

$$Ca (OH)_2 + MgCl_2 \longrightarrow CaCl_2 + Mg (OH)_2 \dots (3)$$

MgSO<sub>4</sub> in SW greatly affects the early hydration of OPC. According to a study done by Zhu et al. (2023), the hydration kinetics of MgSO<sub>4</sub>·7H<sub>2</sub>O and CaSO<sub>4</sub>·2H<sub>2</sub>O in OPC clinker were compared using isothermal calorimetry, chemical shrinkage, and phase

analysis. It was found that MgSO4.7H2O exhibited a stronger retarding effect during the hydration of OPC clinker compared to CaSO4·2H2O; this led to a longer initial and final setting time in the MgSO<sub>4</sub> + Portland Cement Clinker (MPC) system than in the CaSO<sub>4</sub> system (OPC). The combined retardation from Mg (OH)<sub>2</sub>, CaSO<sub>4</sub>·2H<sub>2</sub>O, and other hydration products results in a slower hydration rate for MPC compared to OPC before the deceleration period (Chengyou et al., n.d.) . Furthermore, the MgSO<sub>4</sub> in SW forms magnesium ions, Mg<sup>2+,</sup> which leads to the formation of Mg (OH)<sub>2</sub>. This increases the volume of concrete by approximately 20%, resulting in increased pressure from growing ettringite crystals. This causes surface cracking, known as softening cracks (Zhang et al., 2022).

#### MATERIALS AND METHODS

#### **Raw Materials**

Four cementitious materials were used in this experiment: OPC, PCFA, MSWI, and DG. DG used in this experiment is the by-product gypsum produced by the wet desulphurisation of flue gas in the retorting workshop of Beita Oil Shale Comprehensive Development and Utilisation Co., Ltd.,

OPC was purchased from the Building Materials Research Institute in Beijing.

PCFA was collected after coal-fired power generation in Liaoning port. Its pozzolanic activity comes from the fly ash's rich amorphous Si and Al (Bhatt et al., 2019). These can be hydrolysed in an alkaline environment and combined with calcium hydroxide to form hydrated calcium silicate gel (Mohamed et al., 2021). MSWIFA was sourced from Chengdu, Sichuan, China.

#### Sampling and sample preparation

The raw materials were prepared and dried at 60 degrees Celsius for 24 hours. After drying, they were accurately weighed and divided into five distinct groups, A1-A5. Each group consisted of different proportions of OPC and PCFA, while MSWIFA and DG remained constant at 135 g throughout each group. The table below illustrates the different proportions. Once weighed and grouped, the materials were securely stored in sealed bags to preserve their condition until they were needed for subsequent experiment stages.

Table 1. Composition of raw material in group A1-A5

| Grouping | OPC<br>(g) | MSWIFA<br>(g) | PCFA<br>(g) | DG<br>(g) |
|----------|------------|---------------|-------------|-----------|
| A1       | 90         | 135           | 540         | 135       |
| A2       | 135        | 135           | 495         | 135       |
| A3       | 180        | 135           | 450         | 135       |

| A4 | 225 | 135 | 405 | 135 |
|----|-----|-----|-----|-----|
| A5 | 270 | 135 | 360 | 135 |

Materials from each group were thoroughly mixed, and deionized water was added at 270 g (30 %) for each group. This specific liquid-to-solid ratio was established through preliminary experiments that assessed the solidification time and the mixture's flow properties, which are critical for ensuring uniformity and workability in the casting process.

A homogenous mixed paste was made with a cement mortar blender. It was poured into moulds measuring 3 cm x 3 cm x 5 cm and compacted using a vibrating plate. The resulting blocks were covered with a thin plastic cover to retain moisture and cured in a controlled environment maintained at  $25 \pm 2^{\circ}$ C. Under such curing conditions, we ensured proper hydration to enhance the mechanical properties of the solidified material.

#### Leaching Tests

Leaching test of raw material with deionized water. The raw material's heavy metal content was determined using inductively coupled plasma optical emission (ICP) using deionized water under the standard HJ 557-2010. The heavy metals detected in raw materials are among the 11 heavy metals listed by the national standard, GB 8978-1996.

#### Leaching tests under seawater conditions.

To test leaching in SW condition for each group, an experiment procedure for preparing simulated seawater according to the GB/T 38140-2019 standard, which tests cement resistance to seawater erosion, was carried out. For the leaching test under seawater environment, 10g of each sample was grounded and passed through 100 µm gauze; the larger specific surface area enhances heavy metals' adsorption capacity. This increased surface area allows for more active sites where heavy metals can bind, leading to improved detection accuracy to ensure the best accuracy of heavy metal assessment (Ajorloo et al., 2022) . Following the standard HJ 557-2010, heavy metal was determined under a seawater environment using the simulation seawater solution of seawater (SW). The grounded 10 g of each material from each group was mixed with 100 ml of simulated seawater. To ensure the accuracy of heavy metal leaching, the solution was placed in a shaker machine, set at 110rpm for 8 hours at 25 degrees Celsius, and kept still for 16 hours. The solids were separated from the liquid using a 0.22 µm membrane before being tested with the ICP machines for heavy metal traces.

#### Analytical methods

The concentration of heavy metals in the leaching solvent was analyzed using Inductively Coupled Plasma Mass Spectrometry

X-ray fluorescence spectroscopy Shimadzu XRF-1800 determined the minerals and identified the phases. (Fourier-transform infrared) FTIR USA thermos Fisher Scientific Nicolet iS20 was used.

XRD German Bruker D8 Advanced was used to analyse the materials.

## **RESULTS AND DISCUSSION**

#### The basic shape of raw materials

The raw material of group A1-A5 was tested using XRD to analyze the cementitious properties.



Figure 1. XRD results on the cementitious properties of each group from A1 to A5.

Table 2. Basic properties of each raw material used.

| Ele<br>me<br>nt | OPC<br>(%) | PCFA<br>(%) | MSWI<br>FA (%) | DG<br>(%) |
|-----------------|------------|-------------|----------------|-----------|
| Ca              | 52.044     | 3.611       | 39             | 31.106    |
| 0               | 33.925     | 0.00        | 24             | 45.06     |
| Cl              | 0.181      | 0.059       | 23             | 0.231     |
| Κ               | 0.517      | 0.839       | 4              | 0.078     |
| Na              | 0.155      | 0.423       | 3              | 0.105     |
| S               | 1.139      | 0.353       | 3              | 20.93     |
| Si              | 7.032      | 23.69       | 1              | 0.667     |
| Al              | 1.595      | 17.56       | 0.339          | 0.204     |
| Pb              | 0.00       | 0.015       | 0.075          | 0.00      |
| As              | 0.00       | 0.001       | 0.015          | 0.00      |
| Cr              | 0.00       | 0.011       | 0.013          | 0.00      |
| Cd              | 0.00       | 0.00        | 0.00           | 0.00      |

The desulfurised gypsum's chemical composition mainly consists of CaSO<sub>4</sub>, and its main mineral phase is dihydrate gypsum (Gypsum, CaSO4·2H2O). PCFA had a moisture content of 20 % to 30 %. MSWIFA contained mostly alkaline substances (such as CaO, Na<sub>2</sub>O and K<sub>2</sub>O), so fly ash has a high pH value (pH =12.15; fly ash: water = 1:10 g/ml) and strong acidneutralising ability. Different factors such as garbage composition, incineration conditions, and flue gas treatment processes have led to different compositions of incineration fly ash in various regions of China. The Cl in fly ash comes from the incineration of polyvinyl chloride (PVC) in plastics and sodium chloride (NaCl) in kitchen waste (Kim et al., 2021). The high Cl content limits its use for resource recovery and affects the leaching of heavy metals. In addition, fly ash contains a certain amount of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, which indicates that it can replace part of cement to form cementitious materials (Poranek et al., 2023).

Its main mineral component is  $Ca_3O_5Si$ , which has self-hydrating properties. The hydration reaction produced  $H_2Ca_2O_5Si$  gel and  $Ca(OH)_2$ .

#### **Strength Performance of Low-Cement**

The compressive test was performed after 3, 7 and 28 consecutive days; the results are shown in Figure 2.



Figure 2. Compressive strength of 3, 7 and 28 days. (MPA)

The observed strength test results for cementitious materials with varying proportions of OPC and PCFA indicate a varying relationship between curing time, material composition, and strength development. Groups with a higher amount of OPC gained early strength. The A1 group, which contains the highest percentage of PCFA (66.67 % more than A5), showed delayed strength development. There were no significant strength improvements on days 3 and 7;

however, by day 28, all groups exhibited notable, almost similar value enhancements in strength. During the hydration dynamics, ettringite and calcium hydroxide formation in cement supplemented with coal fly ash enhances strength by promoting hydration reactions that produce (C-S-H) and (C-A-H), resulting in a denser microstructure and high compressive strength (Mohamed et al., 2021).

#### Leaching results

When accessed under normal conditions with deionized water, The leaching test confirmed the raw material's high lead (Pb) levels of 2.317 mg/l.

According to the national standard (GB 8978-1996), lead (Pb) was significantly above the permitted maximum of 1 mg/L. Figure 3 presents the results of heavy metal testing on the materials.



Figure 3. The composition of heavy metals in raw material (Mg/L).

Table 3. Standards (GB 8978-1996) limits(mg/L)

| Elem           | Lead | Arseni | Cadmiu | Chromiu |
|----------------|------|--------|--------|---------|
| ent            | (Pb) | c (As) | m (Cd) | m (Cr)  |
| Limit<br>value | 1.0  | 0.5    | 0.1    | 0.5     |

Using the standard HJ 557-2010, a leaching test was conducted using simulated seawater that was prepared according to standard GB/T 38140-2019. Samples were divided into groups (A1-A5) and categorised based on the number of curing days. XRD and FTIR analyses of the samples indicated an increase in ettringite over the curing period. A significant proportion of ettringite is formed during fast setting when aluminium sulfate combines with calcium and hydroxyl ions generated during hydration, which suggests an increase in strength, supported by a rise in compressive strength over time, as demonstrated by (H. Wang et al., 2024). Heavy metal immobilisation occurred during this hardening period; the ICP analysis confirmed the reduction of heavy metal leaching (Karyappa et al., 2025). The heavy metal analysis conducted at 3, 7, and 28 days of hardening confirmed three heavy metals in low concentration and within the guidelines of the standard (GB 8978-1996) in each group. The ICP results are shown in Figure 4



Figure 4. Heavy metal concentration (MgL<sup>-1</sup>)

#### **XRD** analysis

Calcium hydroxide (Ca(OH)<sub>2</sub>), which can be observed at 18 degrees (2 $\theta$ ), serves as an indicator of ongoing curing; as curing continues, the amount of Ca(OH)<sub>2</sub> decreases. As OPC generates (Ca(OH)<sub>2</sub> while setting, and PCFA reacts with Ca(OH)<sub>2</sub> to form additional calcium silicate hydrates (C-S-H), contributing to the overall strength as illustrated by, This can be explained by the ongoing decrease trend of Ca(OH)2 along group A1-A5 as curing progresses in Figure 5. The implication of decreasing portlandite is a positive attribute of long-term strength and stability (H. Wang et al., 2024). On the other hand, ettringite contributes to the rapid strength gain and accelerates the solidification of heavy metals. In conclusion, the decreasing trend of C a ( O H ) a n d t h e 2





Figure 5. XRD of each group at different curing times.

gradual increase of ettringite during the curing process highlights its key role in hydration dynamics, further evident during the strength test. Group A1 was found to be significantly strong regardless of the 28<sup>th</sup> day of having the most PCFA and less OPC; this can indicate that PCFA reacts with Ca(OH)<sub>2</sub> to produce C-S-H, which improves strength.

#### **FTIR** analysis

Past studies have linked specific absorption bands to particular chemicals. The 3641-3644 cm<sup>-1</sup> range reflects Additional stretching vibrations, indicating a hydration state. 3554 cm<sup>-1</sup> further stresses hydroxyl groups; this wavelength represents the O-H stretching vibrations. The 1640-1650 cm<sup>-1</sup> range reflects bending vibrations associated with a water molecule (H2O), crucial to understanding hydration. While 1417 cm<sup>-1</sup> indicates the wavelength corresponding to the bending vibrations involving hydroxyl groups (O-H), essential for understanding the hydration state in cementitious materials. 970 cm<sup>-1</sup> indicates the stretching vibration of water molecules (H2O) in gypsum, particularly associated with its third overtone vibrational mode (v3). While 875-878 cm<sup>-1</sup> corresponds with the stretching vibration of silicon-oxygen (Si-O) bonds and their behaviour under various situations. 847 to 848 cm<sup>-1</sup> represents chemicals containing sulfur and oxygen. The 811 cm<sup>-1</sup> wavelength represents the symmetric stretching vibration of sulfur-oxygen (S=O) bonds, similar to the sulfonyl group characteristic in many compounds (Feng et al., 2023).





Figure 6. shows the FTIR graphs of each group at different curing times.

 $525 \text{ cm}^{-1}$  represents the deformation of siliconoxygen-silicon (Si-O-Si) bonds, demonstrating how these bonds flex under certain conditions.  $300 \text{ cm}^{-1}$ corresponds to the in-plane bending vibration of silicon-oxygen bonds in silicates (Van Ginhoven et al., 2005).

In this experiment, FTIR analysis was determined in each stage of curing in all five groups; the offset of hydroxyl groups (O-H) around peak 3500 cm<sup>-1</sup> could be explained by the migration of crystallized water, which may affect the environment around hydroxyl groups. The formation of C-S-H is indicated by Si-O stretching peaks, demonstrating its production and contributing to strength, durability, and resistance to chlorine and sulfate attacks, which is particularly important for marine structures. The peaks linked to aluminium silicate Si-O-Al bending vibrations suggest the creation of stable hydration products like ettringite, with the Si-O-Al exhibiting slight shifts at various curing stages, further supporting the idea of ettringite formation. Ettringite is vital in immobilizing heavy metals to prevent environmental pollution and mitigate sulfate attacks to enhance durability (Liu et al., 2023). (C-O stretching) indicates carbonation, where the curing blocks drew carbonation in the atmosphere and incorporated hydration reactions. Several studies have categorised carbonation of cementitious material as vital in improving strength by reacting with calcium hydroxide (Ca(OH)<sub>2</sub> and hydrated silicates to produce CaCO<sub>3</sub>, which improves resistance to porosity. FTIR shows a trend of reduced porosity due to a decrease in water-related peaks. This applies to avoiding chlorine penetration. The presence of sulfate ions (SO42-) plays a significant role in concrete strength; in the early stages of curing, FTIR shows more SO42- peak shift as a result of formation of ettringite the (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O).

In conclusion, the FTIR analysis has demonstrated the hydration dynamics and structural changes in the cementitious material at different curing levels. The development of C-S-H and ettringite greatly improved strength and durability, highlighting their importance.

## CONCLUSION

The study of SCMs has proven to contribute positively to enhancing the performance of cementitious material. (1) SCMs have been proven to positively reduce permeability, especially in marine environments where chlorine and sulphate attacks occur. The results from our experiments show that when PCA is mixed with MSWI FA in the right proportions, it significantly boosts the strength and durability of the cementitious material. During the strength test, it was seen that having more PCFA in a cementitious ratio didn't affect the overall strength. However, it delayed the hardening time.

(2) Overall, this research highlights the promising

the potential of using industrial by-products like MSWIFA and PCFA to create sustainable construction materials while addressing environmental concerns related to hazardous waste.

(3) Heavy metals were immobilized, lowering the concentration below the specified standard limit, regardless of the high lead concentration (Pb) previously found in the raw materials. This reduces the environmental risks associated with heavy metals.

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# EFFECTS OF ELECTRIC FIELDS ON MATURITY AND MICROBIAL DYNAMICS IN SLUDGE COMPOSTING PROCESSES

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#### ABSTRACT

The aerobic sludge composting process, faces a plethora of challenges that significantly impact the compost's ability to mature effectively. Among these obstacles, low temperatures, lengthy fermentation periods, and insufficient material breakdown stand out as key factors that hinder the composting process. These factors are far from optimal for the microbial activity necessary for the efficient decomposition of organic matter. To enhance compost maturity, different electric fields were implemented and compared against composting without an electric field. The introduction of electric fields, particularly at 5V, significantly heightened compost temperatures and prolonged the thermophilic phase, which is crucial for pathogen reduction and compost maturation. The 5V electric field demonstrated superior performance in various parameters. This indicates that the application of electric fields, especially at a higher voltage, can substantially improve the composting process by accelerating the decomposition of organic matter and enhancing the maturity of the compost, which is a critical factor in producing high-quality compost

suitable for agricultural use. Proteobacteria, Firmicutes, Bacteroidetes, and Actinobacteria emerged as the dominant phyla during composting, and electric fields enhanced the relative abundance of Proteobacteria and Bacteroidetes. At the genus level, the application of electric field enriched the compost with key bacterial genera such as Pseudoxanthomonas, known for their role in organic matter decomposition, and promoted the succession of beneficial microbial communities. These findings provide significant understanding and a foundational theory for utilizing electric fields to expedite composting, markedly aiding in the enhancement of the process.

**KEYWORDS:** Aerobic composting; electric fields; Microbial community; Compost maturity.

## **1. INTRODUCTION**

With the urbanization process in China, the amount of urban sewage treatment is increasing, followed by the generation of a large amount of sludge. China boasted 2984 urban sewage treatment plants. The generation of excess sludge with an approximate moisture content of 80% had surpassed  $6.6 \times 10^7$  T in

2022[1-3]. The annual sludge production in China will exceed  $8.0 \times 10^7$  T in 2025[4]. Composting of sludge is one of the effective means of sludge treatment[5, 6]. Sludge aerobic composting treatment can greatly balance the nutrients in sludge[7]. This avoids the pollution of sludge to the environment and turns waste into treasure. However, in the actual aerobic sludge composting, there are often many problems such as low heap temperature, long fermentation period, and insufficient material degradation, which affects the compost maturity[8, 9]. Microorganisms play an important role during composting[10, 11]. Microorganisms rely on oxygen to decompose nutrients, including proteins, polysaccharides, and esters, within organic solid waste. Furthermore, various enzymes secreted by microorganisms can utilize lignocellulose to form small molecules, which ultimately produce stable, humus-rich substances through polymerization[12-14]. Su et al.[15] investigated the role of bacterial metabolic functions in humification and found that amino acid metabolism of bacteria can increase humus content, because bacterial metabolism could affect the enzymatic conversion of organic matter during composting. Zhang et al.[16] incorporated microbial-mediated inoculum (MMI), specifically Bacillus and other species, into the aerobic composting procedure of swine manure. Their findings revealed that the introduction of MMI not only augmented the stability of the compost but also facilitated the nutrient cycling throughout the manure composting process. Meanwhile, Wu et al.[17] have reported that the addition of herbal dregs enhances lignocellulose degradation, while also stimulating carbohydrate metabolism and amino acid metabolism. This effect is achieved by elevating the abundance of bacterial genera, including Acetobacter, Brevundimonas, and Bacillus, as

well as fungal genera such as *Chaetomium*, *Thermacus*, and *Coprinopsis*. Consequently, the study of microbial community succession and metabolic functions during aerobic composting is essential to understand the humification process.

In recent years, composting assisted by electric field has emerged as a significant research focus, aiming to optimize the microbial growth and enhance the composting process. Previous studies have shown that the application of electric field promotes the utilization of oxygen by microorganisms and raises the temperature of composting, thereby promoting the degradation of organic matter and the formation of humus[18, 19]. Tang et al. [20] found that the introduction of a DC electric field increased oxygen utilization by  $30 \pm 9\%$ , while reducing maturation time by 33% in chicken manure composting. Furthermore, the electric field activated key microbial genera, leading to an elevated abundance of Ureibacillus and Navibacillus, thereby enhancing the metabolic activity of the composting system and facilitating the humification of organic matter[21]. Nevertheless, the bulk of composting assisted by electric field has been concentrated on the livestock and poultry manure as composting raw materials [22, 23]. By contrast, the application of sludge composting assisted by electric field remains understudied, and there is a gap in understanding the impact of electric fields on microbial community structure in composting.

This study employed sludge as the primary raw material, augmented with corn stover, and conducted composting experiments under different electric fields. The specific objectives of this study are: first, to investigate the impact of varying electric fields on compost maturity; second, to elucidate the dynamic succession of bacterial communities resulting from the application of an electric field during the composting.

#### 2. MATERIALS AND METHODS

The sludge utilized for the experiment consisted of conventionally dewatered municipal sludge obtained from the Guilin Shangyao Wastewater Treatment Plant. The corn stalks were sourced from local farmers residing near Yanshan Town, Guilin.Three composting reactors, each measuring 45 cm in diameter and 52 cm in height, with a combined volume of 60 liters, were utilized for the composting process. To ensure thermal efficiency, the outer walls of these reactors were encased with 5 cm of insulation material. A rotameter and an air pump were attached to the bottom of the reactors for control of ventilation. DC power supply

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Maturity indexes

Temperature is an important indicator for the degree of decomposition evaluating and harmlessness of compost[25]. As shown in Fig. 1a, the ambient temperature (room temperature) varied little during composting, fluctuating around 30 °C. Three piles CK, A and B entered the high-temperature period (>50 °C) on the first day of composting, and reached the highest temperatures of 62.5 °C, 64.5 °C and 67.1 °C on days 2, 2 and 3, respectively. The temperatures of the piles lasted above 50 °C for 10, 11 and 12 days, respectively and met the hygienic requirements at least 5 days of duration above 55 °C for killing disease-causing microorganisms and weed seeds in the composted material (HJ 1266-2022). The proper increase in voltage raised the temperature and high temperature duration of the high-temperature period. was employed as the power source. A circular 304 stainless steel plate, measuring 120 cm in diameter, 40 cm in width, and 0.3 cm in thickness, was placed along the reactor's inner wall, serving as the positive electrode. Graphite rods, with a diameter of 5 cm and a height of 40 cm, were positioned at the center of the composting pile, serving as the negative electrode. All were configured identically. The composting piles in three reactors were applied DC voltages of 0 V, 2 V, and 5 V, respectively, recorded as CK, A, and B. The municipal sludge and corn stover were mixed in the ratio of 2:1, ensuring a water content approximately 60%[24]. Each bucket of compost is approximately 10 kg. Constant forced aeration was maintained with a flow rate of 0.2 L/ (kg dry-matter•min).

By approximately the 21st day, the temperature had approached ambient levels, indicating the commencement of the maturation stage of the composting process.

The moisture content (MC) is a crucial parameter influencing the composting process, particularly in terms of its impact on the growth and reproduction of microorganisms[26]. During the first fifteen days of composting, the MC of the three piles CK, A and B underwent a significant reduction attributed to the evaporation of water, declining approximately from 60% to 30% (Fig. 1b). By the end of the composting, the MC of the three piles had decreased by 29.8%, 26.3%, and 24.2%, respectively, compared to the initial stages. This observation indicates that that all the piles were mature and stable, which was similar to the previous study[27, 28]. The electrical conductivity (EC) serves as a key metric for assessing the soluble salt content in composting. EC can pose challenges for

plant growth and seed germination when it contains elevated concentrations of soluble salts[29]. As shown in Fig. 1c, the EC values of the three treatments increased from day 0 to day 9, and this increase is thought to be due to the decomposition of organic matter into simple compounds and the formation of organic acids and water-soluble mineral ions (phosphate, calcium, magnesium, potassium, calcium, magnesium). Subsequently, the EC value gradually decreases due to the decomposition of organic acids and the deposition or conversion of various mineral salt ions into gaseous volatiles in the air[30]. The final EC values for the CK, A and B were 1.89, 1.81, and 1.8 mS/cm, respectively. The EC of piles with electric fields is slightly lower than that of pile CK. These values were below the safe application criterion of 4 mS/cm [31].

As shown in Fig. 1d, the pH values of the three piles of CK, A and B increased first and then decreased during composting. The increase of pH from day 0 to day 9 could be caused by the volatilization and decomposition of some organic acids in the composting materials, in conjunction with the decomposition of organic matter during the high-temperature period to produce large amounts of ammonia[32]. Following the day 9, the decline in pH values could potentially be attributed to the conversion of NH4+-N to NO3--N during microbial nitrification[33]. In the heating period of composting, the pH of the pile with electric field was higher than that of the pile without electric field. In the cooling period of composting, the pH of the pile with electric field was lower than that of the pile without electric field. This suggests that the electric field promoted the composting process. At the end of composting, the pH values of the piles of CK, A and B were 6.9, 6.6 and 6.1, respectively, In general, the pH

of the compost has met the recently revised organic fertilizer standard in China (NY525-2021)[28], which coincided with the conclusions drawn by MC and EC.

In general, the greater the decrease of C/N in the composting process, the more the compost tends to mature [34]. The C/N of CK, A, and B decreased by 4.2, 4.57, and 5.03, respectively, during the composting (Fig. 1e). This observation suggests that the application of an electric field with 5V enhanced the maturity of the compost. Typically, compost with a C/N ratio of less than 20 is deemed to be fully composted[35]. The initial C/N of the compost in this experiment was low (all around 10), so T (the ratio of C/N at the end of composting to the initial C/N) can be used to evaluate the degree of compost decomposition. It is deemed that the compost has attained a state of maturity when the compost T <0.6[36]. The T-values of CK, A and B were 0.596, 0.570 and 0.520, respectively, which met the requirements for maturity, and the pile of B had the highest degree of maturity, this suggests that the electric field increased the degree of decomposition of the compost.

The germination index (GI) of seeds is frequently utilized as a metric for assessing the maturity level of compost[37, 38]. Studies have shown that a GI of 50% is considered to be almost decomposed, while 80% is considered to be fully decomposed and not phytotoxic[39]. As shown in Fig. 1f, the GI values of the three piles reached 84.32%, 87.05% and 97.7% respectively, at the end of composting. All of them reached more than 80%, and it can be considered that the three treatments have reached the condition of maturity and the compost products are not phytotoxic[40]. In contrast, the higher GI values of A and B indicated that the electric field promoted the

compost maturation and the maturation of compost was higher when the voltage was higher.



**Fig. 1** Dynamic changes in temperature (a), moisture content (MC) (b), electrical conductivity (EC) (c), pH (d), carbon/nitrogen ratio (C/N) (e), germination index (GI) (f) during composting.

## 3.2 Microbial community succession

the phylum phylogenetic At level, the relationships of bacteria with relative abundance in the top100 for each of the three piles are shown in Fig. 2a. Firmicutes, Proteobacteria, **Bacteroidetes** and Actinobacteria were the dominant bacteria in the composting phase. This is similar to the discoveries of dominant phylum in compost by Wei[41] and Wang[42], which is consistent with the results demonstrated in Fig. 2b.

As shown in **Fig. 2c**, *Proteobacteria* (15.9%-62.0%) were the most abundant, followed by

*Firmicutes* (5.0%-60.6%), *Bacteroidetes* (1.0%-29.6%) and *Actinobacteria* (3.7%-28.3%) in that order. The relative abundance of *Proteobacteria* was significantly higher than the other phyla (37.9%, 34.71% and 42.5% for CK, A and B) at the initial stage (day 0). It was consistently maintained at a high abundance throughout the composting. Interestingly, the abundance of *Proteobacteria* in B was always higher than the other two piles (except for day 9). The abundance of *Firmicutes* reached a peak of 60.5%, 57.1% for CK, A on day 4 and 54.1% for B on day 9 when the composting temperature increased sharply. It can be

inferred from the above results that the abundances of Firmicutes are closely related to temperature, with the similar findings to previous studies. As can be seen in Fig. 2b, the abundance of Firmicutes is 17.1%, 18.6%, and 23.6% in the piles of CK, A, and B. Golnaz reported that the high temperature stimulates the growth of Firmicutes in composting, which can promote the breakdown of proteins, lignin, cellulose, polysaccharides and amino acids in composting. Hence, the application of electric field promotes the growth of Firmicutes during the composting. Both Bacteroidetes and Proteobacteria are able to promote the breakdown of easily degradable small organic molecules, for instances Bacteroidetes are able to break down polysaccharides[42]. They have been shown to play an important role in the compost humification process. The relative abundance of Bacteroidetes was low during the high-temperature phase but high at other phases and peaked at day 30 (12.3%, 16.2%, and 29.6% for CK, A, and B, respectively) (Fig. 2c), proving its intolerance of high temperatures. What is more, the relative abundance of Bacteroidetes was B> A> CK at both the maturation stage and the high-temperature stage, suggesting that the application of electric field can increase the relative abundance of Bacteroidetes.

Furthermore, the 10 genera with the highest relative abundance were also selected for analysis in this study. As shown in Fig. 2d, the genus Pseudoxanthomonas of the phylum Proteobacteria dominated the relative abundance of all three treatments by reaching more than 30%, which is not only heat-tolerant, but also able to mineralize organic matter and nitrogen during composting. Some studies has shown that Pseudoxanthomonas is able to promote the degradation of fulvic acid and humin during composting, resulting in the formation of more humic acid, which demonstrates the ability of Pseudoxanthomonas to promote compost maturation. It is worth noting that the growth of Pseudoxanthomonas, reaching a peak on day 9 of the high-temperature stage. After the 15th day of composting, the relative abundance of Pseudoxanthomonas in A and B were both significantly higher than that in CK, and the relative abundance of Pseudoxanthomonas in B was higher. This precisely indicates that the electric field promotes the increase of Pseudoxanthomonas abundance in the cooling stage and maturation stage of composting, and it increased with the increase of the applied voltage.



Fig. 2 Systematic relationship of phylum horizontal species (a); microbial community composition of samples at the

phylum level (b); microbial community composition of treatments at the phylum level (c); microbial community composition of samples at the genus level (d) during composting.

## 4. CONCLUSIONS

In this study, the applied electric field increased the temperature and prolonged the duration of high temperature during composting. By the end of the composting cycle, the EC values in piles of CK, A, and B were below the safe application standard, and also all the GI values met the conditions of compost decomposition and the compost products were not phytotoxic. These results demonstrate that increasing the voltage from 2V to 5V improved the physicochemical conditions of the composting process and enhanced the degree of compost maturation. Proteobacteria. Firmicutes, Bacteroidetes. and Actinobacteria were the main dominant phyla during sludge composting. Electric field with 5V increased the relative abundance of Proteobacteria and Bacteroidetes in the composting process. At the genus level, the electric field increased the relative abundance of Thermobacillus in the high-temperature phase of the composting and the relative abundance of Pseudoxanthomonas, Niabella and Taibaiella with lignocellulose degrading ability in the cooling and potential maturation phases. The of electric field-assisted composting techniques at different voltages to enhance composting efficiency, improve microbial community structure, and strengthen compost product quality was highlighted in this study, providing perspectives on the optimization new and environmental sustainability of composting processes.

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# EFFECT OF SULFONATING AGENT CONCENTRATION ON SULFONATION TREATMENT OF LAVENDER STALKS

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## ABSTRACT

The primary component of straw biomass, which is a rich renewable resource, is lignocellulose, which includes cellulose, hemicellulose, and lignin. The three components are challenging to use directly, though, because they are strongly interconnected. In order to separate the three components for the straw in the hemicellulose of the subsequent enzyme digestion and straw utilization for convenience, lignin can be converted into hydrophilic lignosulfonate dissolved by treating straw with sulfite. In this study, sulfurous acid, calcium bisulfite, and calcium sulfite were chosen to perform the sulfonation reaction with straw. The effects of sulfonating agent dosage on the sulfonation effect of straw were examined, and the inhibitors and total phenol content of sulfonated solution were ascertained. The substantial amount of waste straw generated following the extraction of essential oil from lavender is a valuable biomass resource. The results showed that the sulfonation impact of straw increased with the rise of sulfonating agent concentration; the sulfite group had more synthetic cellulose degradation and created more sugars, with the maximum total sugar content of 12.84 g/L, but the lignin dissolution was less.

## **1 INTRODUCTION**

Lignocellulosic biomass is the most abundant and inexpensive renewable resource, with a global production of 200 billion tons of lignocellulosic biomass per year, including agricultural waste, forestry waste and cash crops <sup>[1]</sup>. Lignocellulose consists of cellulose, hemicellulose and lignin, which can be hydrolyzed to produce hexose and pentose sugars, which can be converted to ethanol, lactic acid and other volatile compounds by further fermentation. Lignin is a non-sugar component, an aromatic compound composed of three phenylpropane monomers, commonly used in agricultural fertilizers and material products <sup>[2]</sup>. The three components of lignocellulose are cross-linked with each other, which hinders their decomposition and utilization. In order to improve the fermentability of sugars and the application of lignin, pretreatment techniques are usually adopted to separate the three components of lignocellulosic cellulose. Physical pretreatment includes ultrasonic and mechanical treatment, etc., but it is costly, and acid and alkali treatment can effectively release the connecting bonds between the three components, but it requires acidic and alkaline reagents and harsh reaction conditions <sup>[3]</sup>. Sulfite pretreatment is an effective pretreatment method for both wood and non-wood feedstocks (bagasse and straw, etc.) Pretreatment of lignocellulosics enables higher enzymatic efficiency and the level of production of biological growth inhibitors (formic acid, furfural, etc.) is much lower than that of acid treatment techniques <sup>[4]</sup>.

Lignin can be sulfonated to produce lignin sulfonate and dissolved by sulfite pretreatment technology, which can release the cross-linking structure between lignin and cellulose, which is beneficial to cellulose enzymolysis. Lignosulfonate has sulfonic acid groups, and thus possesses water retention and adsorption properties, which can be applied to dispersants, concrete binders, surfactants <sup>[5]</sup>, fertilizers <sup>[6]</sup>, and so on.

Xinjiang is one of the main production areas of lavender in the world, with a sowing area of 43.35 million  $M^2$ . Lavender produces a large amount of waste straw after essential oil extraction, the main component of which is lignocellulose, which is directly discarded, resulting in waste of resources and environmental pollution <sup>[7]</sup>. In this study, lavender straw was selected as the raw material and sulfonated using sulfite pretreatment technology to facilitate the further application of cellulose, hemicellulose and lignin in the straw. The selected sulfonating agent categories were sulfurous acid, calcium sulfite and calcium bisulfite, and the effect of sulfonating agent concentration on the treatment process was investigated.

## 2 MATERIALS AND METHODS

**Straw sulfonation:** 5 g of absolute dry mass of lavender straw was weighed and placed in a reaction vessel, and a certain concentration of sulfonating agent solution was added according to the solid-liquid ratio of 1:8, and then the sulfonation reaction was carried out at a predetermined temperature and time after the reaction was mixed homogeneously. At the end of the reaction, after the temperature of the reaction solution was reduced to room temperature, the solid-liquid separation was carried out, and the liquid was used for subsequent analysis, while the solid was washed, dried

and weighed for the determination of its cellulose, hemicellulose and lignin contents.

Analytical methods <sup>[8]</sup>: cellulose, hemicellulose and lignin contents were determined with reference to the method of the U.S. Department of Energy (NREL); sugar and inhibitor contents were determined using high-performance liquid chromatography (HPLC) on a Shodex Sugar SH1011 column at 60 °C, with a mobile phase of 5 mM H2SO4 at a flow rate of 1.0 mL/min, and with a detector of RID; and total phenol content was determined by the The total phenol content was determined by the forintol method.

## **3 RESULTS AND DISCUSSION**

In this study, lavender straw was sulfonated using calcium sulfite, sulfurous acid, and calcium bisulfite (sulfurous acid+ calcium sulfite), respectively, and the effect of each sulfonating agent dosage on the sulfonated straw was investigated. The dosages of sulfonating agents were 2.5%, 5%, 10%, and 20% (relative to the dry weight of straw), and the reaction temperature was  $120^{\circ}$ C, reaction time 3h, and solid-liquid ratio 1:8.

When lavender straw is sulfonated with sulfites, some of the cellulose and hemicellulose in the straw breaks down into sugars and inhibitors like furfural, acetic acid, and formic acid are produced. Other phenolic compounds are produced together with the sulfonation of the lignin in the straw to lignosulfonates. Inhibitors and phenolics can negatively impact biofermentation and product safety, while sugars and lignosulfonates can be utilized in agricultural fertilizer applications and biofermentation, respectively. Thus, the amount of inhibitors and saccharides in the solution following the straw sulfonation reaction was ascertained in this paper.

# Effect of type and amount of sulfonating agent on sugar content

The results of determining the amount of sugar in the reaction solution of sulfonated straw using three sulfonating agents and varying dosages of sulfonating agents are displayed in Figure 1.



Fig. 1 Sugar content in the reaction solution of sulphonated straw with different sulphonating agent types and sulphonating agent dosages

By altering the quantity of sulfonating agents, the calcium sulfite group showed virtually little change in the amount of sugar in the sulfonated solution (Fig. 1). Since calcium sulfite is an insoluble solid and its insolubility influences the reaction process, the amount of sugar remains nearly constant even if the sulfonating agent dosage is altered during the reaction. As the dosage of the sulfonating agent was raised, more cellulose and hemicellulose broke down into sugars, increasing the sugar concentration in the sulfurous acid group. Although there was not a noticeable change in the sugars in the sulfonated solution of sulfite+calcium sulfite group, the total level was greater than that of calcium sulfite group. As a result, sulfite has a better effect on the breakdown of cellulose and hemicellulose than calcium sulfite. It also produces a bigger amount of sugars; at a dosage of 20%, the sugar content reaches its maximum, totaling 12.84 g/L.

# Effect of type and amount of sulfonating agent on inhibitor and total phenol content

The results of determining the total phenol content and inhibitors in the reaction solution of sulfonated straw using three sulfonating agents and varying dosages of sulfonating agents are displayed in Figure 2. Figure 2 shows that no furfural or 5-HMF was produced in any of the reaction groups, and the amount of formic acid and acetic acid produced was essentially constant. However, as the dosage was increased, the total phenol content in the sulfuric acid group and sulfuric acid+calcium sulfite group increased, and the sulfuric acid+calcium sulfite group's total phenol production was higher than that of the sulfuric acid group overall. As the sulfonating agent dosage increased, more lignin was sulfonated and broken down.



Fig. 2 Inhibitors and total phenol content in the reaction solution of sulphonated straw with different sulphonating agent types and sulphonating agent dosages

#### 4. CONCLUSION

Sulfonation of straw using three different types of sulfonating agents and different dosages of sulfonating agents resulted in a higher sugar content in the sulfonated solution of the sulfite group. The sugar content rose as the sulfite dosage increased, reaching a maximum of 12.84 g/L.

Three different types of sulfonating agents were used to sulfonate the straw; no 5-HMF or furfural were produced, and the amount of acetic and formic acid in the sulfonate remained nearly constant. The total phenol content in the sulfonate rose as the sulfonating agent dosage increased when sulfurous acid and sulfurous acid+calcium sulfite were used as the sulfonating agent types.

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## THE TECHNICAL MECHANISM OF HEAVY METALS IN SOLIDIFIED MUNICIPAL SOLID WASTE INCINERATION FLY ASH

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#### INTRODUCTION

With the fast-paced progress of the economy and society, there exists a considerable volume of household refuse, which would be squandered in dumping grounds. Therefore, in recent years, the incineration of waste has gradually become the mainstream (Fan et al. 2023), and the waste incineration technology is also constantly improving. Currently, waste incineration in China constitutes roughly 65% of the total waste management practices (Song et al. 2023). Incinerating municipal waste can markedly reduce its volume and mass(Hjelmar\* 1996), consequently lessening the space necessary for its disposal (Scarlat et al. 2015, Kundariya et al. 2021). The energy generated through incineration can serve as a source of heat and electricity (Yakubu et al. 2018). However, the incineration of household waste results in MSWI fly ash from municipal solid waste incineration that contains hazardous materials such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), heavy metals, and chlorine salts (Xue and 2021, Nikravan, Liu 2021, Zhang et al. Ramezanianpour and Maknoon 2020).

The number of waste incineration facilities in China rose from 109 in 2011 to 389 in 2019 (Huang et al. 2022). Waste incineration is a significant waste treatment process that has transformed into a primary option for managing increasing municipal domestic waste treatment(Krausova et al. 2016). The treatment capacity rises annually, leading to a substantial increase in MSWI fly ash emissions. In 2020 alone, China produced about 4.43 million tons of MSWI fly ash(Zhang et al. 2022a). The substantial quantity of MSWI fly ash in China presents significant challenges to both the natural environment and land resources (Lin et al. 2022, Yuan et al. 2022). The treatment of fly ash has also become a key issue restricting the development of waste incineration(Bai et al. 2022). During the incineration of household waste, heavy metals undergo several processes, including evaporation, vapor coalescence, particle coalescence, chemical reactions, entrainment of particles (Huang et al. 2022, Hu 2005), and Janus precipitation as illustrated in Figure 1. These are the predominant mechanisms that occur when incinerating domestic waste.



Fig.1 Processes of transformation of heavy metals during the incineration of municipal solid waste.

Cement solidification, chemical stabilization, hydrothermal method(Zhan et al. 2019, Zhan et al. 2022) and melting solidification(Zhan et al. 2021) are the main methods for solidification and stabilization of fly ash (Liu et al. 2022, Zhao et al. 2021b). The cement solidification technique utilizes cement's inherent properties to stabilize heavy metals in MSWI fly ash, forming a product that meets the necessary standards for subsequent treatment and usage (Ma et al. 2019). At present, the research on heavy metals in cement-solidified fly ash is roughly divided into two categories: ordinary cement solidification and ecological cement solidification(Shunda et al. 2022). Pure cement solidification involves the use of specific cement to solidify heavy metals in MSWI fly ash(Zeng et al. 2020). Ecological cement solidification is to use of other solid waste materials to prepare ecological cement and solidify fly ash. The chemical reagent method has the characteristics of low cost, simple and practical, and less or no product compatibilization. It is one of the mainstream methods for fly ash stabilization. This method has gained popularity in recent years due to its many benefits (Ma et al. 2019). Chemical stabilization involves employing chemical agents to bind heavy metals in MSWI fly ash. By coordinating heavy metals within the MSWI fly ash, they form a metal ring structure, effectively fixing the heavy metals. Chemical stabilization methods typically encompass both organic and inorganic methods (Wang et al. 2015b), such as sodium sulphide, sodium dihydrogen phosphate. butylammonium black. ethylenediaminetetraacetic acid (EDTA),

dithiocarbamate (DTC), and other similar options. Compared with the above two methods, hydrothermal method and melting solidification have the ability to degrade dioxins while solidifying heavy metals. Hydrothermal method is another very promising technology for MSWI fly ash treatment (Tong et al. 2022). By modifying the calcium-silica to aluminum-silica ratio in the raw materials, the hydrothermal method can generate silica-aluminate minerals in alkaline conditions. These minerals can then be employed for stabilising heavy metals. Bayuseno and colleagues discovered that hydrothermal treatment of MSWI fly ash can produce different zeolite types that can immobilize heavy metals and greatly decrease their leaching toxicity in MSWI fly ash(Bayuseno, Schmahl and Mullejans 2009). Melting solidification of fly ash is to fully burn the organic components such as dioxins in fly ash at a high temperature(Zhu et al. 2020). The inorganic components in fly ash will be converted into various slags under high temperature conditions. These slags will form a vitreous structure after quenching. A large amount of heavy metal elements in fly ash are blocked in this vitreous structure, so as to realize the solidification of heavy metal elements in fly ash and prevent the transfer of heavy metal elements to the outside world. The solidification/stabilization method glass-ceramics prepared by waste in high of temperature environment has become a more concerned method (Ponsot et al. 2015). In addition to the above four solidification and stabilization methods, of course, some researchers have explored other types of methods, such as Yin Duan 's solidification of MSWI fly ash with MgO-based binder. The results show that the leaching toxicity of MSWI fly ash solidified with MgO-based binder meets the landfill standard and can maintain this low leaching toxicity in a wide pH range (Duan et al. 2023). However, due to the lack of systematic research and more convincing evidence, this paper does not explore these solidification and stabilization methods or mechanisms more.

Based on the existing research, this study systematically summarizes the research progress of various types of fly ash solidification and stabilization in recent years, and analyzes the feasibility and shortcomings of each technology. Finally, the solidification mechanism of various methods for various heavy metals is summarized, so as to determine the most basic research basis of each technology. This information will contribute to the future research on MSWI fly ash solidification and stabilization, and provide corresponding theoretical reference and basis for the treatment of other industrial solid wastes. On this basis, this study will also prospect the solidification and stabilization of fly ash, and further determine the future research direction of fly ash solidification and stabilization.

#### NATURE OF MSWI FLY ASH

The MSWI fly ash produced in the process of municipal solid waste incineration generally presents gravish white powder particles, and the particle size is generally between 1-100 µm. (Yang et al. 2018). Due to the intricate composition of waste, the MSWI fly ash produced from waste incineration typically comprises a substantial quantity of heavy metals. Based on the recent measurements of heavy metal content in incineration MSWI fly ash, it is evident from Fig.2 that MSWI fly ash contains a large amount of Cu, Zn, Pb and a considerable amount of Cr, Ni, Cd. In addition, the fly ash also contains a certain amount of V, Sc, Sn, Sb and other heavy metals (Wang et al. 2023, Marieta, Guerrero and Leon 2021, Yang et al. 2018, Zhang et al. 2023, Xin et al. 2022, Phua et al. 2019, Xu et al. 2019b, Xu et al. 2019a, Long et al. 2021, Zhang et al. 2020).

A study of the physical phase analysis of MSWI fly ash revealed that it is primarily comprised of CaO, SiO<sub>2</sub>,  $Al_2O_3$ ,  $Fe_2O_3$ , SO<sub>3</sub>, Cl, Na<sub>2</sub>O, and K<sub>2</sub>O, which belong to the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> system (Xu et al. 2023, Liu et al. 2018, Li et al. 2021). Due to the high presence of metal oxides and salts, fly ash exhibits alkaline properties(Zhao et al. 2020).

For a large number of heavy metals in fly ash, researchers measured the leaching concentration of heavy metals in fly ash, as shown in Fig.3 (Fan et al. 2021, Cao, Luo and Sun 2021, Fan et al. 2022, Jing et al. 2023, Ma et al. 2023).

Combined with Fig.2, it is evident that while the levels of Zn and Cu in MSWI fly ash tend to be elevated, their leaching concentrations of heavy metals do not exceed the GB16889-2008 pollution control standards for domestic waste landfills. This signifies the feeble leaching toxicity of these two heavy metals. The leaching concentration of Pb is much higher than the standard value, which proves that Pb not only has a considerable content in fly ash, but also has strong leaching toxicity. In addition, the leaching concentration of Cd and Ni is also much higher than the standard value, with strong leaching toxicity.



Fig.2 Literature on heavy metals in MSWI fly ash.

If further action is not taken, an increasing amount of untreated MSWI fly ash will contaminate surface water, soil, and groundwater with notable levels of heavy metal elements. The food chain will transport these contaminants, eventually presenting a risk to human health and safety. Hence, technologies for solidifying and stabilizing fly ash are continually progressing.



MSWI fly ash in different literature.

### STATUS OF RESEARCH ON CURING MSWI FLY ASH TECHNOLOGY Cement curing MSWI fly ash

MSWI fly ash exhibits certain volcanic ash properties, and it can elicit a corresponding volcanic ash reaction. An analysis of the fly ash composition shows that it belongs to the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> oxide system, which can react with calcium hydroxide. If the system contains a higher concentration of CaSO<sub>4</sub>, it will produce a binder known as calcium aluminate (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>-26H<sub>2</sub>O), while lower levels of CaSO<sub>4</sub> can result in the production of calcium (Aubert, carbon-aluminate  $(Ca_8Al_4O_{14}CO_2-24H_2O)$ and Sarramone.2006). Husson Calcium aluminosilicates are commonly found in amorphous and crystalline forms, and their small particle size allows for the facilitation of chemical reactions(Zhou et al. 2017). Kai Wu et al. have recognized cement as a highly effective and promising solution for MSWI fly ash disposal and resource recovery from an environmental recycling standpoint. It has been extensively utilized for solidifying and stabilizing hazardous components (Wu et al. 2012). Therefore, the production of cement clinker is a promising technology for the reliable and economical treatment of MSWI fly ash.

Ordinary Portland Cement(OPC), is а non-homogeneous mixture that typically is manufactured by heating a blend of clay and limestone to around 1450°C (Chen et al. 2009). Single OPC has demonstrated efficacy in the immobilization of heavy metals. Jiang-Shan Li and colleagues examined the impact of ordinary Portland cement (OPC) on leaching in soil contaminated with lead (Li et al. 2014a). It was discovered that the concentration of lead ions leached decreased by a substantial 34.9 % when the ratio of water to soil was heightened from 0.2 to 0.4. Tome et al. found that when the ratio of silicate-based cement to fly ash was 1:1, the compressive strength of the solidified body was still 10.5 MPa after 28 days of curing, and the

leaching concentration of heavy metals was reduced to varying degrees(Tome et al. 2018). In another study, Oluwatuyi and colleagues (year) found that the incorporation of OPC boosted soil products' adsorption capacity for Pb contaminants (Oluwatuyi, Ashaka and Ojuri 2019). Fei et al. reported similar observations. They carried out experiments, and the results showed that OPC (8wt %) had good stability for Cd and Zn, and the solidification rates were 99.9 % and 99.4 %, respectively (Fei et al. 2018).

## Chemical stabilization of MSWI fly ash

The chemical technique has become a prominent method for stabilizing heavy metals in MSWI fly ash owing to its affordability, simplicity of operation, and minimal or negligible capacity increase (Xue and Liu 2021, Du et al. 2019). Depending on the chemical stabilization agents utilized , inorganic, organic, and hybrid stabilization can be categorized(Wang et al. 2015b).

In the present chelating agent market, inorganic chelating agents are more economical. However, the effectiveness of using inorganic chelating agents for the stabilization of heavy metals in MSWI fly ash is unsatisfactory(Shunda et al. 2022), resulting in a high leaching concentration of several heavy metals. Although organic chelating agents are effective at stabilizing heavy metals, their expensive cost and selective chelation of heavy metals make it difficult to ensure the stabilization of all heavy metals. Therefore, a combination of organic and inorganic chelating agents was used for treatment. The application of a blend of appropriate inorganic and organic agents to MSWI fly ash can extend the duration of stabilization and improve outcomes, while also promoting good product expansion and yielding economic advantages(Zhao et al. 2022).

Jiemin Zhu et al (Zhu et al. 2020) developed both single and combined stabilizers to handle the fly ash produced by waste incineration. The comparison of treatment outcomes revealed that, while a single agent with a certain concentration may release heavy metals to the environment within the specified limits, the mixed-agent method is more efficient and less expensive than single-agent treatment. Most of the effective organic chelators are manufactured or patented in laboratories, resulting in their high costs.

Therefore, utilizing the complementary properties of various chemicals widely available in the market can facilitate the attainment of necessary stability for diverse metals to curtail expenses. This is an optimal resolution to the predicament of balancing chelation cure efficiency and expense.

## Hydrothermal solidification of MSWI fly ash

The principle of hydrothermal solidification of MSWI fly ash is to fix heavy metals in fly ash by mixing fly ash with the corresponding alkali solution and having a hydrothermal reaction at a certain temperature (Panek et al. 2021). According to the hydrothermal solidification process whether or not to add auxiliaries in the hydrothermal method here will be divided into ordinary hydrothermal method, microwave hydrothermal method and the addition of auxiliary hydrothermal method.

Ordinary hydrothermal method is to mix MSWI fly ash with a certain amount of lye, and then heat it by ordinary heating source, so that the internal hydrothermal reaction occurs, and then filtering and drying steps to get the final reaction product. In this process,(Hu et al. 2015) the silica aluminum calcium oxides inside the MSWI fly ash will generate mineral salts such as zeolites during the heating process, and these mineral salts have the effects of wrapping, adsorption, exchange and precipitation for the heavy metals in the fly ash, so that the heavy metals are stabilized in these mineral salts and prevented from leaching out of the heavy metals.

The research on the proof of the corresponding mineral salts produced by hydrothermal reaction of MSWI fly ash can be traced back to 1998, Yang et al. (Gordon C.C. Yang 1998) found that after hydrothermal treatment of MSWI fly ash, silica-aluminate minerals with good stabilization effect on heavy metals were produced. In addition, by controlling the conditions of the hydrothermal reaction, minerals such as chalcocite and zeolite were produced, and this research evidence directly proves that MSWI fly ash can be converted into zeolite and other minerals to be used to solidify heavy metals in fly ash. After Yang, some scholars have studied the products of the hydrothermal reaction of MSWI fly ash; Muelle jans et al. (Bayuseno et al. 2009) obtained large quantities of katoite and chalcocite by placing MSWI fly ash in a 0.5 mol/L NaOH solution and heating it at 180°C for 48 h. The study also showed that the MSWI fly ash can be transformed into zeolite and other minerals to solidify the heavy metals in fly ash.

Jin et al (Jin et al. 2009, Zhang et al. 2022) used simulated wastewater mixed with MSWI fly ash and added sodium carbonate as an alkaline exciter, and found that the leaching concentration of heavy metals in the final hydrothermal product was reduced and lower than the leaching standard for hazardous wastes in China by performing a hydrothermal reaction.

The microwave hydrothermal method is based on the ordinary hydrothermal method, the heat source of ordinary hydrothermal method is replaced by microwave for heating. Compared with the traditional water heating method, microwave hydrothermal method has the advantages of fast heating speed, high heating efficiency, energy saving and cost reduction(Yuan et al. 2023).

Qiu et al. (Qiu et al. 2016) heated at 125 °C for 25

min with 1 mol / L NaOH solution and a liquid-solid ratio of 7 : 2, the leaching concentrations of all heavy metals except Cd were lower than the pollution control standard limit of China 's domestic waste landfill . Compared with the original MSWI fly ash, it has better environmental adaptability. Compared with the traditional hydrothermal method, (Qiu et al. 2016) the researchers found that the energy consumption of microwave hydrothermal method is only 1/3 of the original hydrothermal method, which is more energy efficient and environmentally friendly. The use of microwave hydrothermal method can basically make the leaching of waste incineration fly ash lower than the limit value of China's domestic waste landfill pollution control standards, and the reaction time is greatly shortened to only 20 min, which greatly improves the efficiency of the use of hydrothermal method to solidify heavy metals in MSWI fly ash. Zhiwen Xu et al. solidified the heavy metals in MSWI fly ash by microwave hydrothermal method. After treatment, the leaching concentrations of Cr, Ni, Cu, Zn, Pb and Cd in MSWI fly ash can meet the specified limits of GB16889-2008(Xu et al. 2023). In order to further improve the effect of microwave hydrothermal fixation of heavy metals, a certain amount of phosphate can be added appropriately. The effect of microwave hydrothermal method on fluidized bed fly ash and grate furnace fly ash is excellent. The microwave hydrothermal method with fast speed, good effect and good universality(Li et al. 2019) is worthy of further development.

In order to further enhance the effectiveness of hydrothermal methods for the solidification of heavy metals in MSWI fly ash, researchers have achieved this process by adding additional additives. The addition of silica-aluminum additives and crystal seed additives promote the production of more silica-aluminum mineral salts to solidify heavy metals (Zhang et al. 2022b). Addition of ferrous and phosphates on the other hand promotes the synthesis of alkaline iron salts with alkaline calcium phosphate to stabilize the heavy metals(Hu et al. 2015).

## Thermal treatment of MSWI fly ash

The main categories of heat treatment are vitrification(Gao et al. 2020), melting(Yue et al. 2019) and sintering(Zhan et al. 2021). The distinction between heat treatment methods is based primarily on the characteristics of the process product rather than the process itself. In vitrification, a glassy phase is produced, while in melting, crystallization or heterogeneous products are formed by melting ash or residues. In sintering, the residue is heated to achieve reconfiguration of the solid material (Lindberg, Molin and Hupa 2015). In order to prevent chloride ions from combining with heavy metals at high temperatures to produce the more hazardous and difficult to immobilize

heavy metal chlorides, MSWI fly ash is generally washed to remove the chloride ions during high temperature curing. The sintering method is generally at a temperature of about 700-1000  $^{\circ}$ C, the use of fly ash in the calcium and silicon and other elements to produce ceramic particles. It has been shown (A.A. Kudyba-Jansen 2001) that the mechanical properties of silicon-based ceramics synthesized by carbon thermal synthesis of fly ash are comparable to those of silicon-based ceramics made from clay and pure oxides.

Some of the hazardous metals in the MSWI fly ash, such as Cd, Pb, Hg, etc., are vaporized during thermal treatment, and these heavy metals are no longer detectable in the sintered product after treatment(Lindberg et al. 2015). Some organic pollutants also decompose during thermal treatment. Chen (Chen, Wang and Tang 2010) produced lightweight aggregates from MSWI fly ash by sintering in a commercial rotary kiln with an outer diameter of 2 meters and a length of 39 meters using heavy oil as fuel. Based on their results, it was shown that light meeting the density aggregates and toxicity requirements could be produced at 30% addition of MSWI fly ash. Xinyuan Zhan et al. used MSWI fly ash to prepare ceramsite. When the temperature exceeded 1160 °C, the leaching toxicity and risk of heavy metals in ceramsite were greatly reduced(Zhan et al. 2023).

MSWI fly ash vitrification is a method of removing dioxins from fly ash at temperatures above 1000 degrees Celsius and using the resulting glass network to solidify heavy metals in the fly ash (Quina, Bordado and Quinta-Ferreira 2008). In the glass network structure, certain metals form covalent bonds with oxygen and essentially act as network formers, while others form ionic bonds with oxygen and act as network modulators. Some ash components may also be encapsulated in the glass during cooling of the glass melt, protecting these components from chemical attack and limiting their ability to escape from the glass (Lindberg et al. 2015). In order to improve the stability of this glass network, some additional additives containing silica are usually added.

Young Jun Park (Young Jun Park 2002) obtained inert glasses containing high concentrations of hazardous metals by adding at least 10 wt% SiO<sub>2</sub> and 10 wt% MgO. According to their results, it was found that vitrification was very effective in reducing the toxicity of Cr, Cd and Pb in MSWI fly ash. Chuanwei Li et al. successfully prepared CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glass-ceramics by using lead-zinc tailings and coal gangue. The toxicity evaluation of heavy metals in all samples met the requirements of EPA and CN GB 5058.3(Li et al. 2023a).

However, due to the characteristics of vitrification technology that requires high temperature, it is bound to consume a large amount of energy, in order to solve this problem, in recent years, researchers have tried to reduce the energy consumption by adding some co-solvents. Zhao et al. found that the addition of K2O and Na<sub>2</sub>O can significantly reduce the sintering temperature when sintering ceramsite(Zhao et al. 2021a). Huang Qunxing et al (Huang et al. 2014) used wood ash as a co-solvent to reduce the melting temperature of waste incineration MSWI fly ash and calculate its heat of fusion, the results show that when adding 50% of the mass ratio of wood ash, the melting temperature of MSWI fly ash was reduced by nearly 300  $^{\circ}$ C, and its heat of fusion was reduced by about 700 kJ/kg. Ma Wenchao et al (Ma et al. 2017) used SiO<sub>2</sub> as a co-solvent, and the SiO<sub>2</sub>: MSWI fly ash was 1:1.39. The results show that the melting temperature of MSWI fly ash was decreased by nearly 300 °C, and its heat of fusion was decreased by about 700 kJ/kg. The results showed that the melting temperature of MSWI fly ash was reduced by nearly 800°C from more than 2200°C to 1450°C.

High-temperature solidification technology in addition to the need for higher temperatures and energy consumption of this problem, the low added value of its slag is also worth considering, these are the current high-temperature solidification technology is urgently needed to resolve the problem.

## CURING MECHANISM OF HEAVY METALS FROM MSWI FLY ASH CURING

## Physical adsorption and encapsulation

Physical adsorption and encapsulation is to block the second condition mentioned above, the principle is to use the dense molecular structure produced by the solidified body and the solid shell of the solidified body itself to adsorb and encapsulate heavy metal ions to prevent them from overflowing as shown in Fig.4(Zhan et al. 2022).

Physical encapsulation is present in the four main methods of solidified heavy metals in MSWI fly ash, including cement solidification of heavy metals in fly ash, hydrothermal solidification of heavy metals in fly ash and high-temperature solidification of heavy metals in fly ash. In these three types of solidified methods after solidification are produced more dense and low-permeability of these solidified bodies, due to these solidified bodies for the heavy metals in the fly ash for a full range of coverage and package so that the heavy metals and the external environment to isolate the heavy metals, heavy metal leaching toxicity is greatly reduced(Li et al. 2023b). In addition, these solidified bodies will also produce various types of cyclic molecular structure, these molecular structures will produce closed network structure cavity (Tian et al. 2019), which will encapsulate toxic substances such as heavy metals, and further reduce the leaching toxicity of heavy metals(Pan et al. 2019).



Fig.4 Schematic diagram of physically encapsulated heavy metals.

#### **Chemical reaction**

If physical encapsulation is to isolate heavy metals from the outside world on a large scale greater than or equal to the molecular level, then chemical reaction is to achieve the solidification of heavy metals through blocking conditions 1 by fixing heavy metals on a smaller scale, that is, at the atomic level, against the attraction of other environments to heavy metals. Chemical reactions can be divided into precipitation reactions, ion exchange reaction, chelation reaction and redox reaction depending on the reaction principle(Guo et al. 2019, Ji and Pei 2019, Wong et al. 2020).

In the study of heavy metals fly ash solidified by cement, cement will undergo hydration reaction after encountering water. Dicalcium silicate and tricalcium silicate will produce a large amount of hydrated calcium silicate in the hydration reaction, while tricalcium aluminate will produce ettringite (AFt) and hydrated calcium chloroaluminate. The main reaction formula is as follows (Chen et al. 2009):

 $\begin{aligned} 3(3\text{CaO} \bullet \text{SiO}_2) + 3\text{CaSO}_4 + 32\text{H}_2\text{O} &= 3\text{CaO} \bullet \text{Al}_2\text{O}_3 \bullet \\ 3\text{CaSO}_4 \bullet 32\text{H}_2\text{O} \end{aligned} \tag{3}$ 

 $\begin{aligned} 3CaO \bullet SiO_2 + CaCl_2 + 10H_2O &= 3CaO \bullet Al_2O_3 \bullet CaCl_2 \bullet \\ 3CaSO_4 \bullet 10H_2O \qquad (4) \end{aligned}$ 

C-S-H (3CaO·2SiO<sub>2</sub>·3H<sub>2</sub>O) is an amorphous colloidal substance (Czop et al. 2022). It has a large specific surface area, so it can physically adsorb heavy metals to fix a part of heavy metals. For example, the fixation of  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$  is the process of adsorption of C-S-H on it(Shao et al. 2013b). After  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$  enter the C-S-H, they will exchange with the calcium through ion exchange, occupying the position of the original calcium ion to achieve a relatively stable state ;  $Cr^{3+}$  will replace the silicon in the silicon-oxygen tetrahedron in the system, occupying the position of the original silicon, and use K<sup>+</sup> to balance the charge (Tian et al. 2019); the hydroxide ions and silicate ions in

C-S-H will turn Zn into  $Zn(OH)_2$  and  $Zn_2SiO_4$  precipitates, and then these precipitates will be wrapped by hydrated calcium silicate gel to form physical encapsulation to prevent the leaching of heavy metals.



several heavy metals.

3CaO-Al<sub>2</sub>O<sub>3</sub>-3CaSO<sub>4</sub>-32H<sub>2</sub>O, namely ettringite (AFt), as another major substance in the hydration products of cement, also plays a very important role in the immobilization of heavy metals(Aubert et al. 2006). The molecular structure of ettringite is shown in Fig.6, its molecular structure presents a cylindrical shape with Al connecting with six OH to form  $Al(OH)_6$  presenting an octahedral structure as the center of the cylinder, Ca connects four H<sub>2</sub>O and four OH- through hydroxide ions and Al connected to the composition of the cylinder . In order to balance the charge, the cylinder contains a certain amount of sulfate ions within the interior. The cylindrical structure of ettringite is special, in which Al and Ca can be replaced by other metal elements to undergo ion exchange reaction. Heavy metals such as Pb, Cu and Zn in incineration fly ash will replace part of Al and Ca in ettringite through ion exchange reaction and be fixed inside ettringite. The heavy metal Cr generally forms a negative acid ion, so it will exchange with the hydroxide ions in the ettringite and the sulfate ions used to balance the charge to enter the interior of the cylinder and be fixed(Zhou et al. 2017). Studies have shown that (Chrysochoou and Dermatas 2006), many heavy metal cations can enter the ettringite lattice to undergo ion exchange reactions, but ettringite has poor solidified effect on the coexistence of multiple heavy metals, and is not resistant to high temperature and freeze-thaw cycles ; in addition, the sulfate ions in ettringite can be replaced by similar negative metal ions, and the negative metal ions will be fixed in the channel of ettringite needle-like structure after replacing the sulfate ions.


Fig.6 Molecular structure model of ettringite.

In addition, another product of cement hydration, 3CaO-Al<sub>2</sub>O<sub>3</sub>-CaCl<sub>2</sub>-3CaSO<sub>4</sub>-10H<sub>2</sub>O (Friedel's salt), has also been shown to have a good immobilization effect on heavy metals (Jiang et al. 2022). Friedel's salt is a lavered composite metal hydroxide, which has been widely used in the removal of heavy metals such as Pb, Cd, and Cu due to its special structure, large specific surface area, good stability, and excellent ion-exchange performance (Rojas 2014). Friedel's salt cures heavy metal ions mainly by anion exchange and surface adsorption (Zhang et al. 2013). Studies has shown that some oxidation ions such as CrO<sub>4</sub><sup>2-</sup>, SeO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup> can enter the Friedel's salt lattice by substituting Cl-(Min et al. 2019, Shao et al. 2013a). In addition, studies have shown that compared with C-S-H and ettringite, Friedel 's salt has a better solidification effect on heavy metals, the resulting product is more stable, and its immobilization efficiency is also higher (Zhang et al. 2013).

The mechanism of using chemical agents to solidify heavy metals in MSWI fly ash is mainly to utilizes a series of reactions between chemical agents and heavy metals, including precipitation reaction, coordination chelation reaction and so on(Sun et al. 2019). The reaction process is shown in Fig.7.



Fig.7 Reaction process of heavy metal solidification by chemicals

Inorganic chemical agents are mainly associated with various heavy metals in fly ash to produce compounds with low toxicity and low solubility through precipitation reaction. Common precipitations include sulfide, hydroxide and phosphate precipitation of heavy metals(Luo et al. 2022). A study (Jin et al. 2023) carried out mechanochemical pretreatment of fly ash by using several different inorganic agents and according to its results, the composite additive (50% NaH<sub>2</sub>PO<sub>4</sub> + 50% CaO) had the best inhibitory effect on heavy metals, and the leaching concentrations of Cd, Cr, Cu, Ni, Pb and Zn decreased by 95.21 %, 46.84 %, 99.42 %, 49.91 %, 99.83 % and 99.55 %, respectively.

Organic chemical reagents mainly make use of the strong electronegativity and large atomic radius of the O, N and S atoms within some organic substances to form coordination chelation with heavy metals, generating strong coordination bonds and stable polymer chelate precipitates, thus immobilizing the heavy metals. Organic molecules form strong polar bonds with heavy metals through O, N and S as strong coordination centers. electronegative Different chelating agents and different heavy metal chelating products in the structure is a certain difference, but the most basic stabilization mode is the same, such as Fig.7, are through the chelating agents above the effective functional groups and heavy metal ions to occur chemical bonding cooperation to produce a stable crosslinked network structure to stabilize the heavy metals.

The mechanism of hydrothermal solidification of MSWI fly ash is in an alkaline environment at a temperature of 200 °C or so(Shi et al. 2016), fly ash or the addition of additives in the silica-aluminum substances react to produce the corresponding alkaline environment of the ions are generally silicate and meta-aluminate, and then the two further react to produce the corresponding gel. The gel will further precipitate to form a crystal nucleus. When the precipitate crystal nucleus is formed, as the reaction progresses, the amorphous aluminosilicate gel gradually agglomerates as a nucleus, slowly encapsulates and grows into a new crystal until the silicon and source in the reaction system are exhausted. The growth of the crystal was terminated. The specific steps are shown in Fig.8.

Some of these crystal minerals produced in hydrothermal reactions stabilize heavy metals by using heavy metals as crystal nuclei to wrap them inside the crystal, such as hydrocalumite. Some have formed a porous three-dimensional cage-like network structure composed of  $[SiO_4]$  and  $[AIO_4]$  with strong electronegativity to adsorb heavy metal ions into the cage-like structure for stability, such as zeolite minerals such as tobermorite and glauberite. Some heavy metals are captured by silicate minerals by ion exchange reaction (Bukhari et al. 2015, Li et al. 2014b, X. Querol 2002). In conclusion, in either case, heavy metals can be well stabilized.



Fig.8 Mechanisms of heavy metals in hydrothermally cured MSWI fly ash.

Dioxins are currently known to have the strongest toxicity. The treatment of dioxins in fly ash has always been a key issue in inhibiting the treatment and disposal of fly ash. At present, the known treatment method of dioxins is high temperature heat treatment(Gan et al. 2021). At a temperature of about 800 °C, dioxins exist for no more than two seconds. The heavy metals in fly ash treated by high temperature melting and solidification can effectively decompose dioxins in fly ash while solidifying heavy metals(Li et al. 2023c). In the high temperature environment above 1000 °C, the organic matter such as dioxins in the fly ash will decompose instantaneously. The large amount of Ca, Si, Al and other elements contained in the fly ash will form an amorphous solid glass phase at high temperature, while the heavy metals will be completely wrapped by the glass phase in different forms to prevent its leaching(Zhang et al. 2021, Guo et al. 2017a, Guo, Shi and Huang 2017b).

As shown in Figure 9, the glass phase produced by the fly ash at a temperature above 1000 ° C will wrap some of the heavy metals, while the other part of the heavy metals will react to form a series of compound salts, and the latter part will enter the glass phase and be completely wrapped in (Lindberg et al. 2015). the other part is the ion with the same size and charge as the heavy metal in the substitution crystal, which becomes a stable microcrystalline phase in the system, such as the formation of mullite and pyroxene phase(Zhang et al. 2016b). Finally, the system is slowly cooled and formed while the heavy metals are all encapsulated in the high-temperature molten product, which can be ceramic, ceramsite or glass-ceramics.



Fig.9 MSWI fly ash melt curing mechanism diagram.

#### CONCLUSION

This study mainly summarizes and summarizes the solidification methods and mechanisms of heavy metals in four kinds of fly ash, and draws a new mechanism diagram of four kinds of solidification methods according to the description of each paper and reasonable inference, which provides reference for subsequent research. However, the solidification technologies of incineration fly ash are still not very mature at present, and there are many problems in the application of these technologies:

1.Cement solidified fly ash: the subsequent treatment of solidified body and whether it can be stored for a long time without causing new pollution problems.

2.Chemical stabilization: cost and whether it can be used on a large scale, whether the long-term curing effect is stable and the problem of dioxins.

3.Hydrothermal solidification: the treatment cost is high, the decomposition of dioxin is generally 75 % -85 %, and the water-soluble salt is not utilized.

4. High temperature melting curing: high energy consumption, high cost, complex equipment operation and maintenance.

These problems still need researchers to continue to explore and solve.In addition, in the current research stage, although the research mechanism of each fly ash solidification technology is more or less presented and reasoned out, the clear process of many technical mechanisms and the specific behavior under the micro level are still unable to be studied and obtained. The mechanism of each technology is still being explored and improved, and even the mechanism model of fly ash solidification of various heavy metals and the quantitative analysis of solidified products still need to be established and improved. In the future, these are the things that researchers should first consider and carry out.

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# Influence of freeze-thaw cycles and wet/dry alternation on the leaching behavior of solidified/stabilized MSWI fly ash

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#### INTRODUCTION

In recent years, with the acceleration of urbanization in China, the urban population has continued to grow, leading to a significant increase in the production of municipal solid waste. This trend has posed increasing challenges to residents' quality of life and urban management, making the issue of "waste encircling cities" increasingly prominent and urgent to address. Statistics show that in 2019, the total amount of municipal solid waste generated in large and medium-sized cities nationwide reached 235.6 million tons, with a treatment volume of 234.87 million tons. The primary disposal methods included composting, landfilling, and waste-to-energy incineration. Municipal solid waste incineration(MSWI) technology has emerged as the most effective method for achieving the reduction, resource recovery, and harmless treatment of urban waste, and has been widely promoted and applied(Tian et al., 2023; Z. Zhang et al., 2023).

During the process of municipal solid waste incineration, the presence of significant amounts of moisture, organic matter, and inorganic impurities in the waste results in the generation of two types of ash: bottom ash and fly ash. Bottom ash, which constitutes approximately 80% of the total ash produced, primarily consists of glass, ceramic, metallic fragments, and other non-combustible materials as well as partially combusted organic substances. In contrast, fly ash accounts for about 20% of the total ash and is composed of particulates captured by the air pollution control (APC) system, materials collected in the heat recovery system, and bottom ash settled at the base of flue ducts and chimneys. Fly ash is considered hazardous waste due to its high content of chlorides, heavy metals (including zinc, lead, cadmium, nickel, copper, mercury, and arsenic)(Chen et al., 2022; B. Wang & Fan, 2020), and organic compounds such as dioxins and furans. With an annual production exceeding tens of millions of tons(Xin et al., 2023), the safe and efficient treatment of fly ash has become an urgent research priority in China(Sun et al., 2016). Currently, landfill disposal is the predominant method

for handling fly ash. However, direct landfilling poses significant risks of groundwater and soil contamination. Therefore, pre-treatment to render fly ash non-hazardous is necessary before landfilling can be conducted safely.

Current treatment methods for municipal solid waste incineration fly ash primarily include washing and separation, thermal treatment techniques, and solidification/stabilization (S/S) technology, with the latter being one of the most widely used approaches in China(Quina et al., 2014). Initially developed for managing radioactive waste, S/S technology, including cement-based and chemical agent-based stabilization, is now extensively applied to the treatment of hazardous waste(Tang et al., 2020). Cement-based S/S involves the addition of binders (such as Portland cement and lime) to immobilize toxic components through physical and chemical means, thereby reducing the mobility of heavy metal ions. This method is favored for its simplicity and low cost(Lam et al., 2011); however, the high chloride content in fly ash can disrupt the cement hydration process(Du et al., 2019). Additionally, the technology faces challenges such as high volume expansion ratios, limited heavy metal immobilization capacity, and long-term environmental risks(Fan et al., 2021; Jiang et al., 2022). Chemical agent-based S/S, which employs inorganic or organic reagents to stabilize heavy metals in fly ash, offers better stabilization performance but comes with higher treatment costs and greater susceptibility to environmental conditions(Vavva, n.d.). To address the limitations of using either solidification or stabilization alone, the combined use of cement and organic chelating agents for fly ash treatment has been shown to lower treatment costs, reduce volume expansion, and significantly enhance the immobilization of heavy metals, making it easier to meet landfill disposal standards. This combined approach is considered an effective and widely adopted S/S technology in China(Ma et al., 2019; Y. Wang et al., 2022).

However, there are still unresolved issues with solidification/stabilization (S/S) technology. For instance, it is commonly believed that fly ash S/S

matrices buried in landfills over the long term are subject to continuous environmental changes. Therefore, the long-term stability of fly ash S/S matrices remains unclear. Freeze-thaw cycles (FTC) and dry-wet cycles (DWC) are critical for evaluating long-term stability, as alternating exposure to rain and sunlight can affect fly ash S/S matrices after landfill disposal(Gong et al., 2016; He et al., 2019). Studies have shown that freeze-thaw conditions may also be encountered under landfill disposal scenarios. Frost action is one of the most significant factors negatively impacting the structural durability of cement-based materials(Deniz & Erdem, 2021; F. Wang et al., 2021). During DWC, the continuous structural damage to fly ash S/S matrices can lead to heavy metal dissolution, thereby reducing the long-term stability of municipal solid waste incineration fly ash. Consequently, further assessment of long-term effects is necessary.

This study primarily investigates the changes in heavy metal leaching concentrations and occurrence forms of fly ash solidification/stabilization (S/S) matrices under extreme conditions, such as freeze-thaw cycles and dry-wet alternation, as the number of cycles increases. The mineral composition and functional group variations of the fly ash S/S matrices were characterized using X-ray diffraction (XRD). The study further evaluates the impact of chelating agent types and concentrations, as well as cement content, on the chelation-solidification treatment of fly ash, and assesses whether such treatments pose environmental risks under extreme conditions.

#### MATERIALS AND METHODS

#### Sampling and sample preparation

The municipal solid waste incineration fly ash used in this study was sourced from an incineration plant in Chengdu, Sichuan Province, China, employing a grate-type incinerator. The collected raw fly ash was dried at 85°C for 24 hours and then sieved through a 40-mesh screen for storage. The chemical elemental composition of the fly ash samples was analyzed using X-ray fluorescence (XRF) spectroscopy, with the results presented in Table 1. The heavy metal organic chelating agents used in the experiments were TS300 (piperazine dithiocarbamate), procured from Tosoh Corporation, Japan, and domestically produced SDD (dithiocarbamate). The solidifying agent employed in the experiments was commercially available ordinary Portland cement (42.5R grade).

Table 1. Basic properties of the MSWIFA.

| <br>          | -       |         |         |        | ~ .    |        |        |
|---------------|---------|---------|---------|--------|--------|--------|--------|
| elemental⇔    | Ca⇔⊐    | Cl⇔     | O←⊐     | K←⊐    | Na⇔    | S←⊐    | Si⇔    |
| percentage/%⇔ | 30.949⇔ | 28.792⇔ | 22.109↩ | 6.218↩ | 5.31↩  | 2.519↩ | 1.171↩ |
| elemental⇔    | Fe⇔     | Zn⇔⊐    | Mg⇔     | Al⇔    | Ti⇔    | P←⊐    | Pb←⊐   |
| percentage/%⇔ | 0.81←   | 0.497↩  | 0.453⇔  | 0.37⊲  | 0.289⇔ | 0.147↩ | 0.126  |

The selected chelation-solidification matrices for the freeze-thaw and dry-wet alternation tests were composed of 1.8 wt% TS300 and 25 wt% cement (1.8T+25C), 2.3 wt% TS300 and 15 wt% cement (2.3T+15C), and 3 wt% SDD and 25 wt% cement (3S+25C).

#### Leaching tests

With reference to the requirements of the Chinese standard Solid Waste-Leaching Toxicity Leaching Method-Acetic Acid Buffer Solution Method (HJ/T 300-2007), the leaching of MSWI FA before and after stabilization was simulated in the environment of a mixed landfill of domestic waste after leaching by refuse leachate; the leaching solution was acetic acid with pH = 2.64. Finally, the HM concentrations in the leaching solution were analyzed using inductively coupled plasmaatomic emission spectrometry (ICP-AES) according to the Chinese standard method Waste-Determination 22 metallic Solid of elementsInductively coupled emission plasma spectrometry (HJ 781-2016).

With reference the standard Solid to Waste-Leaching Toxicity Leaching Method-Sulfuric Acid Nitric Acid Method (HJ/T 299-2007), the leaching of MSWI FA before and after its stabilization was simulated in a parti tioned landfill environment after acid rain drenching, with leaching agent pH = 3.20 $\pm$  0.5 (H2SO4: HNO3 = 2:1). Finally, the HM concen trations in the leaching solution were analyzed using ICP-AES according to the Chinese standard method 22 Solid Waste-Determination of metallic elements-Inductively coupled plasma emission spectrometry (HJ 781-2016).

#### Analytical methods

X-ray fluorescence spectroscopy (PANalytical Axios) was used to determine Chemical composition(W. Zhang et al., 2021). Water content was determined by standard method (GB 7172-1987), and heavy metal concentration in the leaching solvent was determined by ICP-MS (NexLON350X, PerkinElmer, USA), each test was performed in triplicate(X. Wang et al., 2020)

#### **RESULT AND DISCUSSION**

#### Effects of Freeze-Thaw Cycles on Heavy Metal Leaching Behavior in Fly Ash Solidified/Stabilized Bodies

Fig. 1 shows the morphology of representative 3S+25C solidified body specimens after 0, 3, 6, 9, and 12 freeze-thaw cycles. Observations indicate that with an increasing number of freeze-thaw cycles, the solidified body gradually disintegrated. Cracks began to appear after 3 cycles, and by the 12th cycle, the solidified body had completely disintegrated. The

fragmentation of the solidified body significantly increased the contact area between the fly ash and the external solution, leading to a decline in the C-S-H gel's ability to adsorb and immobilize heavy metals(Zhongping et al., 2021).



Fig. 1. 0, 3, 6, 9, 12 freeze-thaw cycle morphology

Leaching tests were conducted on solidified bodies subjected to 12 freeze-thaw cycles using sulfuric acid-nitric acid buffer solution method (HJ/T299-2007) and acetic acid buffer solution method (HJ/T300-2007). The leaching concentrations of heavy metals Zn, Pb, and Cd from the three fly ash solidified/stabilized bodies are shown in Fig. 2. According to the standards set by the Chinese Municipal Solid Waste Landfill Standard (GB 16889-2024), the permissible concentrations in the leachate for Zn, Pb, and Cd using the acetic acid buffer solution method are 100 mg/L, 0.25 mg/L, and 0.15 mg/L, respectively. For hazardous waste landfill pollution control (GB 18598-2019), the permissible concentrations using the sulfuric acid-nitric acid buffer solution method are 120 mg/L, 1.2 mg/L, and 0.6 mg/L for Zn, Pb, and Cd, respectively. The following discussion refers to the GB 16889-2024 standard due to its stricter limits.

As shown in Fig. 2a, Fig. 2b, and Fig. 2c, the leaching concentrations of Zn, Pb, and Cd for the three solidified bodies after 12 freeze-thaw cycles under HJ/T299 did not exceed the permissible limits. Similarly, Fig. 2d shows that Zn leaching concentrations under HJ/T300 also remained within the limit. However, in Fig. 2e, the Pb concentration for the 3S+25C solidified body exceeded the limit at the 3rd cycle, reaching 0.32 mg/L, but subsequently returned to compliance in later cycles. In Fig. 2f, the Cd concentration for the 1.8T+25C and 2.3T+15C solidified bodies using the TS300 chelating agent exceeded the limit at the 3rd freeze-thaw cycle. The 3S+25C solidified body maintained compliance for the first 9 cycles, but at the 12th cycle, the Cd concentration surged to 1.27 mg/L, exceeding the limit by 8.47 times. The Cd leaching concentrations for the 1.8T+25C and 2.3T+15C solidified bodies were 0.47 mg/L and 0.42 mg/L, respectively, exceeding the limit by 3.13 and 2.8 times, indicating a significant increase in the leaching risk of 3S+25C.

Overall, after 12 freeze-thaw cycles, all samples exhibited an increase in Zn, Pb, and Cd leaching concentrations to varying degrees. The 3S+25C solidified body showed particularly pronounced heavy metal leaching, while the 1.8T+25C body had comparatively smaller increases. This suggests that the SDD chelating agent's resistance to extreme low-temperature environments is weaker than that of the TS300 agent, leading to increased environmental risks associated with heavy metal leaching. Therefore, in practical landfill environments, it is recommended to immediately cover and seal the fly ash chelation-solidified bodies with a membrane and add a soil insulation layer to mitigate the impact of extreme low temperatures.



Fig. 2. Freeze-thaw cycle leaching toxicity

The changes in heavy metal occurrence forms in fly ash chelation-solidified bodies before and after freeze-thaw cycles were investigated using the BCR sequential extraction method. The changes in the occurrence forms of heavy metals Zn, Pb, and Cd at the 0th, 3rd, and 12th freeze-thaw cycles are shown in Fig. 3, where the x-axis FT0 represents the 0th freeze-thaw cycle, and so on. Fig. 3a,Fig. 3b, and Fig. 3c on the left illustrate the occurrence forms of heavy metals Zn, Pb, and Cd in the original incinerated fly ash. It was found that the proportion of acid-soluble (F1) and reducible (F2) states was significantly higher in untreated fly ash, indicating a high risk of heavy metal leaching and emphasizing the importance of pre-treatment.

Among the three concentrations, the combination of TS300 chelating agent and cement performed better than the combination of SDD chelating agent and cement. Although the addition of TS300 was lower, the proportion of easily leachable components (F1+F2) for Pb and Cd in the 3S+25C solidified body, which is a combination of 3 wt% SDD and 25 wt% cement, was significantly higher. After 12 freeze-thaw cycles, the reducible state (F2) of Cd even reached 95.1%. For Zn, the changes in heavy metal forms were not significant before and after treatment with the chelating agents and cement, and the proportion did not show significant changes with freeze-thaw cycles. For Pb, the chelation and solidification treatment greatly increased the oxidizable and residual fractions, and the changes in heavy metal forms were not substantial with increasing cycles. For Cd, the freeze-thaw cycles had a greater impact on the solidified body, particularly for the 3S+25C solidified body, where the proportion of the oxidizable state increased from 60.8% before the cycles to 95.1% after 12 cycles, indicating a high leaching risk.



Fig. 3. Freeze-thaw cycle BCR heavy metal morphology

The XRD results for the mineral phases of the three concentrations of fly ash chelation-solidified bodies after 12 freeze-thaw cycles are shown in Fig. 4. The primary mineral phases in the solidified bodies include NaCl, KCl, CaCO<sub>3</sub>, CaSO<sub>4</sub>·2H<sub>2</sub>O, and CaSO<sub>4</sub>, with the most prominent peaks being those of the soluble chlorides NaCl and KCl, due to the high chlorine content in the fly ash. After freeze-thaw cycles, all samples exhibited some degree of mineral phase change: the peaks of NaCl and KCl gradually weakened, indicating that the structural breakage of the solidified bodies due to freeze-thaw cycles allowed water vapor from the external environment to dissolve the soluble salts through cracks.

During the initial 3 cycles, characteristic peaks of CaSO4 were still observed in the solidified bodies; however, after 12 cycles, the CaSO<sub>4</sub> peaks disappeared, replaced by CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) peaks, indicating that CaSO<sub>4</sub> underwent hydration due to water exposure. Additionally, an increase in the CaCO<sub>3</sub> peak was observed, suggesting that the fragmentation of the solidified body allowed some CaSO<sub>4</sub> to be converted to CaCO<sub>3</sub> due to CO<sub>2</sub> exposure.



Fig. 4. Freeze-thaw cycling XRD mineral composition

#### Effects of Wet-Dry Alternation on Heavy Metal Leaching Behavior in Fly Ash Solidified/Stabilized Bodies

Fig. 5 shows the morphology of representative 3S+25C solidified body specimens after 0, 3, 6, 9, and 12 wet-dry alternations. Observations indicate that while the surface of the solidified bodies showed slight peeling during the wet-dry cycles, the overall morphology did not change significantly, and the overall structure remained intact. This partially explains why the impact of freeze-thaw cycles on the heavy metal leaching toxicity of chelation-solidified bodies is greater than that of wet-dry cycles.



Fig. 5. 0, 3, 6, 9, 12 wet-dry alternations morphology

Leaching tests were conducted on solidified bodies subjected to 12 wet-dry alternations using the sulfuric acid-nitric acid buffer solution method (HJ/T299-2007) and the acetic acid buffer solution method (HJ/T300-2007). The leaching concentrations of heavy metals Zn, Pb, and Cd from the three fly ash solidified/stabilized bodies are shown in Fig. 6. Similar to the results of chelation-solidified bodies subjected to freeze-thaw cycles, the leaching of heavy metals using the sulfuric acid-nitric acid buffer solution method did not exceed the permissible limits. The Zn concentration in the acetic acid buffer solution method also remained below the limit; however, as shown in Fig. 6e, the Pb concentration in the 3S+25C solidified body exceeded the limit during the 3rd cycle, reaching 0.31 mg/L, but subsequently returned to compliance in later cycles. As shown in Fig. 6f, the Cd leaching concentration of the

3S+25C solidified body reached 0.91 mg/L after the 12th wet-dry alternation, exceeding the limit by 6.01 times. The 1.8T+25C and 2.3T+15C solidified bodies with TS300 chelating agent slightly exceeded the limit during the 3rd wet-dry alternation, and after 12 cycles, the Cd leaching concentrations reached 0.39 mg/L and 0.53 mg/L, exceeding the limit by 2.6 and 3.53 times, respectively.

In summary, after 12 wet-dry alternations, the leaching concentrations of Zn, Pb, and Cd in all chelation-solidified bodies increased to some extent, with the 3S+25C solidified body showing the highest heavy metal leaching, while the 1.8T+25C solidified body had a relatively smaller increase. Notably, the heavy metal leaching concentrations of the fly ash chelation-solidified bodies after wet-dry alternation were lower compared to those after freeze-thaw cycles. This indicates that the leaching risk of heavy metals in fly ash chelation-solidified bodies is higher in freeze-thaw environments However, wet-dry alternation still affects the chelation-solidified bodies to some extent. Therefore, it is recommended to and immediately cover seal the flv ash chelation-solidified bodies after landfill to prevent rainwater infiltration, which can lead to wet-dry alternation. If mixed with municipal waste, proper leachate collection and drainage systems should be installed.



Fig. 6. Wet-dry alternations leaching toxicity

The BCR sequential extraction method was used to explore the changes in the occurrence forms of heavy metals in fly ash chelation-solidified bodies before and after wet-dry alternation. The changes in the occurrence forms of heavy metals Zn, Pb, and Cd at the 0th, 3rd, and 12th wet-dry cycles are shown in Fig. 7, where the x-axis label DW0 represents the 0th wet-dry cycle, and so forth.

The results indicated that after 12 wet-dry alternations, the leaching risk of heavy metals in fly ash chelation-solidified bodies increased. For the 1.8T+25C solidified body, the proportion of easily leachable components (F1+F2) increased from 67.5% to 71.0% for Zn, 0.66% to 0.68% for Pb, and 35.3% to 37.1% for Cd after 12 cycles compared to before the cycles. For the 2.3T+15C solidified body, these components

increased from 65.7% to 69.8% for Zn, 0.18% to 0.67% for Pb, and 12.57% to 35.3% for Cd. For the 3S+25C solidified body, the proportion of easily leachable components increased from 68.7% to 70.1% for Zn, decreased from 8.7% to 7.7% for Pb, and increased from 60.8% to 90.5% for Cd. Comparing these results with those of freeze-thaw cycles, it was found that the increase in easily leachable components after 12 wet-dry alternations was lower, corroborating the experimental findings that heavy metals are more prone to leaching under freeze-thaw conditions. This suggests that changes in extreme temperature conditions have a greater impact on the stabilization of heavy metals in fly ash chelation-solidified bodies than changes in extreme humidity conditions. Additionally, it is noteworthy that adding more TS300 effectively reduced the proportion of easily leachable components; however, as wet-dry alternation progressed, these components showed a significant increasing trend. For the 1.8T+25C solidified body with less TS300 chelating agent but more cement, the change in the occurrence form of Cd was not significant, similar to the trend observed in freeze-thaw cycles. This indicates that adding more ordinary Portland cement can effectively help the stabilization of heavy metals in chelation-solidified fly ash resist changes in temperature and humidity, thus reducing the risk of heavy metal leaching. The hydration reaction of cement produces alkaline substances such as C-S-H and Ca(OH)<sub>2</sub>, which not only enhance the strength of the solidified body, improving the encapsulation of heavy metals and aiding in resistance to extreme environmental conditions, but also increase the alkalinity of the solidified body, promoting the binding of heavy metals with the cement matrix, making them less soluble and reducing their mobility(Du et al., 2019; Liu & Shi, 2022).



Fig. 7. Wet-dry alternations BCR heavy metal morphology

The XRD results for the mineral phases of the three concentrations of fly ash chelation-solidified bodies after 12 wet-dry alternations are shown in Fig. 8. The primary mineral phases include NaCl, KCl, CaCO<sub>3</sub>, CaSO<sub>4</sub>, and Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O. Similar to the results of freeze-thaw cycles, NaCl and KCl showed the strongest peaks, which gradually decreased with the progression of wet-dry alternation, with a greater reduction compared to freeze-thaw cycles. It is particularly noteworthy that the characteristic peak of Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O (Friedel's salt) appeared during the 3rd wet-dry alternation. Its formation results from the reaction between Cl- and calcium aluminate hydrates, which can immobilize Cl- and heavy metal ions in the matrix, reducing their mobility. Additionally, higher Cl- concentrations and humidity levels promote the formation of Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O. It can be inferred that wet-dry alternation facilitated the formation of Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O, thereby enhancing the ability of the fly ash chelation-solidified body to immobilize heavy metals. This is one reason why the heavy metal leaching concentrations under wet-dry alternation were lower compared to those under freeze-thaw cycles.



Fig. 8 Wet-dry alternations XRD mineral composition

#### CONCLUSION

This study aims to investigate and discuss the long-term leaching risk, heavy metal occurrence forms, and mineral composition of fly ash chelation-solidification matrices under extreme conditions such as freeze-thaw cycles and dry-wet alternation. The following conclusions were drawn:

(1) After 12 freeze-thaw cycles, the leaching concentrations of Zn, Pb, and Cd in all samples showed varying degrees of increase, with the 3S+25C sample exhibiting particularly pronounced heavy metal leaching, whereas the 1.8T+25C sample showed relatively smaller increases in leaching concentrations. In the BCR test, although the TS300 addition was lower,

the proportion of easily leachable fractions (F1+F2) for Pb and Cd in the 3S+25C sample was significantly higher. After 12 freeze-thaw cycles, the reducible state (F2) of Cd even reached 95.1%. In the XRD analysis, the peaks of NaCl and KCl gradually weakened, and after 12 cycles, the CaSO<sub>4</sub> peak disappeared, replaced by the CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) peak.

(2) After 12 dry-wet cycles, the leaching concentrations of Zn, Pb, and Cd in all solidified matrices showed varying degrees of increase, with the 3S+25C sample exhibiting higher heavy metal leaching concentrations, while the increase in the 1.8T+25C sample was relatively smaller. The addition of more TS300 effectively reduced the proportion of easily leachable components in the solidified matrices; however, as the dry-wet cycles progressed, there was a significant increasing trend in the easily leachable fractions. In contrast, the 1.8T+25C matrix, containing less TS300 and more cement, showed no significant change in the occurrence forms of Cd. The dry-wet cycles promoted the formation of Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O, which enhanced the ability of the fly ash chelation-solidification matrices to immobilize heavy metals.

(3) The leaching risk of heavy metals from fly ash chelation-solidification matrices is higher under freeze-thaw cycle conditions, although dry-wet alternation also has a certain impact on these matrices. Changes in extreme temperature conditions have a greater influence on the heavy metal immobilization effectiveness of fly ash chelation-solidification matrices compared to changes in extreme humidity conditions. The addition of more ordinary Portland cement can effectively enhance the resistance of the heavy metal occurrence forms in the chelation-solidification matrices to temperature and humidity variations, thereby reducing the risk of heavy metal leaching.

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# CONSTRUCTION AND VALIDATION OF A SEMI-THEORETICAL AND SEMI-EMPIRICAL MODEL FOR STATIC DRY ANAEROBIC LIQUID-LI QUID MASS TRANSFER IN A CAPILLARY STRUCTURE ENHANCED B Y SYNERGIZING LEACHING AND AIR PRESSURE FLUCTUATION

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#### ABSTRACT

The aim of this paper is to solve the problem that the traditional static dry anaerobic technology through the leacha te reflux is difficult to change the low efficiency of mass transfer in the capillary pore channel. In this study, a semi-t heoretical and semi-empirical model was established based on the simple model of stainless steel capillary capillary e nhanced by leaching and pressure fluctuation through theoretical deduction, model modification and experimental ve rification. Based on this model, the range of air pressure fluctuation during the anaerobic reaction process was deter mined by combining the economy and enhanced mass transfer efficiency. The results showed that the air pressure fluctuation range was  $\pm 10$ kPa and the mass transfer efficiency was increased by 11.88%. The model proposed in this pa per provides a new idea to solve the contradiction between the traditional static dry anaerobic solid content and mass transfer efficiency, and strongly supports kitchen waste harmless and resourceful treatment and industry carbon emiss ion reduction.

#### 1. Introduction

Kitchen waste, which usually has a solids content of between 20% and 35%, is a high-solids biomass waste and is suitable for dry anaerobic treatment. However, C hina's dry anaerobic treatment technology has not been applied in mature engineering, currently are using forei gn commercial dry anaerobic technology, such as DRA NCO, VALORGA, KOMPOGAS, etc. Due to the paten t limitation, the investment and operation cost of the ab ove technologies are still high with the investment of ab out 700,000 yuan for the ton treatment scale and the op erating costs of about 600-800 yuan<sup>[1]</sup>, which makes it d ifficult to popularize the application. The composition o f kitchen waste material in China is complex and has gr eat difference, so the imported technologies have many problems, such as long system debugging time, unstabl e operation and low gas production rate. Therefore, the

research and development of new dry anaerobic treatme nt technology with low investment, stable operation and high efficiency, which is adapted to the characteristics of kitchen waste in China, is of decisive significance to promote the China's strategy of classifying municipal s olid waste.

High solid content is the most essential characteristic of dry anaerobic treatment technology and the key fact or limiting its development<sup>[2]</sup>. Compared to the wet ana erobic technology in which the material is fluid or semi -fluid, the dry anaerobic system with high solid content has solid material and less free water<sup>[3]</sup>. In the static dr y anaerobic technology without external disturbance, po or mixing, low homogenization, and unsatisfactory syst em mass transfer are more prominent due to the charact eristics of high solids content of the material, which inc reases the risk of feedback inhibition in the static dry an aerobic system, and reduces the system gas production and gas production rate.

Stirring is often used to improve the mass transfer eff iciency im dry anaerobic reaction system, so that the ga s-liquid-solid three-phase distribution in the matrix is u niform, reduce the occurrence of extreme reaction envir onment<sup>[4]</sup>. The common stirring methods include bioga s reflux stirring, biogas slurry reflux stirring and mecha nical stirring<sup>[5, 6]</sup>. Biogas reflux agitation<sup>[7]</sup> is achieved b y collecting and pressurizing the biogas produced insid e the reactor and then agitating the solids inside the reac tor by high pressure gas, as in the case of the VALORG A process using 800 kPa. The cost of this method is hig h, and the effect of high pressure on microorganisms in the reactor needs further study. The biogas slurry reflux stirring<sup>[8]</sup> refers to adding the biogas slurry reflux in the dry fermentation process, which can maintain the suita ble moisture content of the substrate in the fermenter, at the same time, biogas slurry was used as media to stren gthen the re-mixing and distribution of substrate, micro organisms, and the liquid phase in different regions, and to improve the uneven distribution of substrate. Xu<sup>[9]</sup> u sed dry rice straw and pig manure with TS more than 2 0% as raw materials and compared three ways of no ref luxing, refluxing every day, and refluxing with two-pha se method. He found that the biogas slurry reflux could wash and dissolve the local accumulated acid between t he substrates to the filtrate, which can obviously impro ve the gas production rate. Biogas slurry reflux stirring is less costly, simple to operate and easy to maintain, bu t due to the uneven microbial concentration in the ferme ntation system, and the path of the biogas slurry reflux i n the fermentation system is cured, some dead zones sti ll exist. Mechanical stirring is carried out through the in stallation of impeller and other stirring equipment in the reactor. The dynamic seal of the stirring shaft complica tes the structure of the reactor, while the solid material acts on the stirrer with higher resistance, resulting in a h igher power input<sup>[5, 6, 10]</sup>. Although mechanical stirring<sup>[1</sup> <sup>1]</sup> is considered to be the most effective ways of enhanci ng mass transfer efficiency, its long-term operational sta bility is not as good as that of biogas reflux stirring and

biogas slurry reflux stirring [12].

In addition, researchers have proposed novel stirring methods such as pressure pulsation to improve mass tra nsfer efficiency in a stable and efficient manner<sup>[13]</sup>. Li<sup>[14]</sup> put forward the concept of pressure pulsation in solid medium fermentation, which enhanced biological reacti on and intra- and extracellular transfer processes throug h external cyclic stimulation. That is, with the gas as dy namic, and the solid medium as the static, through the p ressure fluctuation of the gas phase, achieving the contr ol and uniformity of temperature and humidity on the s mall scale around the bacteria, as well as the discharge of gas<sup>[15]</sup>. Peng<sup>[16]</sup> introduced the pressure pulsation into the anaerobic system, and adopted the pressure control measures to improve the feedstock gas production rate of dry fermentation. This measure directly produced me thane-rich biogas with CH<sub>4</sub> content up to 80%, and the maximum daily yield was 62.55 ml/gVS, which was 29. 64% higher than that of atmospheric fermentation. How ever, it has also been pointed out that with the high pres sure and periodic air pressure fluctuation, the water con tent of solid substrate decreases obviously<sup>[17]</sup>, which aff ects the growth of microorganisms, and the rapid releas e of high pressure will cause some damage to the mycel ium, affects the reaction rate. In addition, high pressure biogas reflux stirring and pressure pulsation represented by the VALORGA process rely on high positive pressu re, which requires high pressure resistance on the reacti on equipment and auxiliary facilities such as pipeline, makes it more difficult to use and maintain in practice. I f the peak pressure can be reduced by alternating positi ve and negative pressure, and the effect of low-pressure stirring can be achieved under the condition of keeping a certain pressure difference, it will be beneficial to pro mote its practical application.

In summary, dry anaerobic process is affected by ma ny factors. During the actual operation, the changes of a ll factors should be considered comprehensively, and th e process parameters should be optimized through the monitoring of relevant indicators, so as to improve the s tability of the dry anaerobic system and the performanc e of gas production.

In order to solve the problems of poor mass transfer a nd severe local acid inhibition in the static dry anaerobi c system, the development of a new static dry anaerobic technology adapted to the characteristics of the compo nents of China's kitchen waste, and with low investmen t, stable operation, and high efficiency has great signific ance. To achieve this, this study proposes the leachate c ycle synergistic pressure fluctuation static dry anaerobi c technology, carries out related basic research around t his technology. In this study, a semi-theoretical and sem i-empirical model of enhanced mass transfer efficiency based on real materials was established by studying the law of liquid-liquid mass transfer enhanced by leaching and air pressure fluctuation through a simple model of stainless steel capillary tube, the suitable range of press ure fluctuation and the effect of enhanced mass transfer were determined.

### 2.Experimental equipment, materials and methods 2.1 Composition of experimental equipment

The experimental equipment for leaching synergistic pressure fluctuation is a four-unit cylindrical leaching r eactor with the same specification fixed on the acrylic b ase (Fig. 2.1). Every two reactors are connected in paral lel to share a set of air pressure fluctuation system, each reactor is equipped with a separate set of water distribu tion system, and the four reactors are parallel experime ntal group, their air pressure fluctuation and water distribution condition are the same.



(a) Schematic diagram of four cylinder leaching reactor



(b) Physical diagram of four cylinder leaching reactor

# Figure 2.1 Schematic diagram and physical diagram of four cylinder leaching reactor

**2.1.1 Leaching Reactor:** In this experiment, a cylindri cal leaching reactor with a double-layer cylinder structur re was designed, and the inner cylinder could be removed in one piece. The top of the outer cylinder is a flange blind plate, which is provided with a water inlet and a pressure sensor interface. The inner cylinder of the reactor adopts the stainless steel dirt intercepting basket of the washing pool, which is placed on the plum-shaped u niformly perforated filter plate at the lower part of the outer cylinder of the reactor, and the experimental materials are packed in the inner cylinder (Fig. 2.2).



Figure 2.2 Schematic diagram of the structure of the lea ching reactor

2.1.2 Air Pressure Fluctuation System: The two ax isymmetric reactors in parallel share a pressure fluctuati on system (Fig. 2.3). Manual valves are provided on ea ch branch pipe to open and close the pipeline. The air in let manifold of the two reactors is connected to the outl et of the fan by an equal diameter tee, and the extractio n manifold is also connected to the fan inlet by an equal diameter tee, so as to realize the simultaneous control o f the two reactors by a single fan. The fan is a small adj ustable-frequency centrifugal fan, which can change the fluctuation value of the air pressure in the reactor by ch anging the rotating speed. Simultaneous positive and ne gative air pressure fluctuations in both reactors can be a chieved by switching valve combinations. Take negativ e pressure as an example (Fig. 2.3(b)), when the two rea ctors need to be switched to negative pressure, open the fan, valves of extraction manifold and exhaust manifol d, and close the valves of air inlet manifold and air supp ly pipe, so that the fan pumping away the gas inside the two reactors and then discharged by the exhaust branch

pipe, to realize the two reactors synchronized to achiev e the negative pressure state.



(a) Schematic diagram of positive air pressure fluctuati on system condition



(b) Schematic diagram of negative air pressure fluctuati on system condition

Figure 2.3 Schematic diagram of reactor air pressure flu ctuation

**2.1.3 Water Distribution System:** Each reactor is equi pped with a separate water distribution system (Fig. 2. 4). The system consists of peristaltic pump, inlet hose, outlet hose, ultra-pure water distribution tank and leach ate collection tank. Because the two systems of water di stribution and air pressure fluctuation run simultaneousl y, the outlet hose is shut off by the water stop during the period of air pressure fluctuation. The leachate in the in let tank is pumped into the reactor by the peristaltic pu mp through the inlet hose, the leached liquid is tempora rily stored in the reactor under the filter plate, and the li quid level is ensure fluctuation is over, the water stop is opened, and the leachate flows through the outlet hose t

o the leachate collection box for collection.



Figure 2.4 Schematic diagram of water distribution syst em

#### **2.2 Experimental materials**

Stainless steel capillary tubes and stainless steel solid tubes (Table 2.1) were used as filling materials for the simple model liquid-liquid mass transfer enhancement e xperiment (Fig. 2.5). The mixture of kitchen waste and straw (Table 2.2) was used as the filling material for the liquid-liquid mass transfer enhancement experiments (Fig. 2.6), and the real material was crushed to a particl e size of  $\leq$ 5mm.

Table 2.1 Stainless steel pipe size table

| Num. | Туре              | Outer Dia<br>meter R/m<br>m | Inner Diam<br>eter r/mm | Length<br>L/mm |
|------|-------------------|-----------------------------|-------------------------|----------------|
| SS0  | Solid Tube        | 3                           | -                       | 10             |
| SS1  | Capillary<br>Tube | 3                           | 1                       | 10             |



Figure 2.5 Simple model stainless steel capillary



Figure 2.6 Manual allocation of kitchen waste raw mate

rials

Table 2.2 Manual allocation of kitchen waste ingredients ratio (measured by wet weight)

|                 |         |         |          |         | υ       |        | (       | 5      | υ,      |          |
|-----------------|---------|---------|----------|---------|---------|--------|---------|--------|---------|----------|
| Compon          | Chhage  | Lettuce | Carrot P | Corn Co | Apple S | Banana | Chicken | Cooked | Cooking | Rice Str |
| ents            | Coblage | Lettuce | eel      | bs      | kin     | Skin   | Breast  | Rice   | Oil     | aw       |
| Propotio<br>n/% | 18      | 18      | 8        | 8       | 7       | 7      | 8       | 15     | 1       | 10       |

#### **2.3 Experimental methods**

2.3.1 Liquid-liquid mass transfer experiments in c apillary structures with a simple model synergistical ly enhanced by leaching and air pressure fluctuation s: A simple capillary structure model was constructed with stainless steel capillary stack, with chlorine ion as mass transfer efficiency indicator and stainless steel soli d stack as control. Through the above way to get the liq uid-liquid mass transfer efficiency of the capillary struc ture in the stainless steel capillary stack under a certain air pressure fluctuation. And compared with the efficien cy under normal pressure, the experimental value of liq uid-liquid mass transfer efficiency enhanced by a certai n air pressure fluctuation is obtained, and the theoretical model is modified accordingly.

The cycle of each experiment was 5 min. The four in ner tubes of the reactor containing the stainless steel ca pillary stack, which were soaked in sodium chloride sol ution for 12 hours and drained of the gravity water, wer e placed on the filter plate in the reactor, and then seale d the outer tubes and clamped the outlet hose with a wa ter stop, the four reactors are in parallel groups. Subseq uently, according to table 2.3 of the air pressure fluctuat ion in order to leaching co-pressure fluctuation experim ent. Ultra-pure water was used as the lysate for the who le process through the peristaltic pump. At the end of ea ch 5 min experiment, the water stop was opened to coll ect the leachate from the stainless steel capillary tube. T he operation was repeated in the corresponding four rea ctors with the stainless steel solid tube stack as the cont rol.

According to the different air pressure fluctuation val ues set in table 2.4, the accuracy of the modified model is verified by the above experimental data. The experim ental operation is the same as above.

Table 2.3 The experimental parameter setting was modi

1.1 . 6.1.

0

+2

0

-2

0

C 11 - 4

SS1

**SS0** 

0.1

S1(0)

 $S_{0(2)}$ 

|      | ned by | y the simp                   | ple r  | nodel     | of liqui              | a         |        |
|------|--------|------------------------------|--------|-----------|-----------------------|-----------|--------|
| Grou | Тур    | Liquid<br>surfac             | Va     | lues of a | air press<br>ges /kPa | sure in s | sta    |
| р    | e      | e load∕<br>m∙h <sup>-1</sup> | t<br>1 | t2        | t3                    | t4        | t<br>5 |
| Som  | SS0    |                              |        | 0         | 0                     | 0         |        |

0

0 -2

| S <sub>1(2)</sub>  | SS1 | -2  | +2  | -2  |  |
|--------------------|-----|-----|-----|-----|--|
| $S_{0(4)}$         | SS0 | -4  | +4  | -4  |  |
| $S_{1(4)}$         | SS1 | -4  | +4  | -4  |  |
| S <sub>0(6)</sub>  | SS0 | -6  | +6  | -6  |  |
| $S_{1(6)}$         | SS1 | -6  | +6  | -6  |  |
| S0(8)              | SS0 | -8  | +8  | -8  |  |
| $S_{1(8)}$         | SS1 | -8  | +8  | -8  |  |
| S <sub>0(10)</sub> | SS0 | -10 | +10 | -10 |  |
| $S_{1(10)}$        | SS1 | -10 | +10 | -10 |  |

Table 2.4 The simple model of liquid circulation and pr essure fluctuation verifies the experimental operation p

| arameter setting |
|------------------|
|------------------|

| Grou              | Tuno | Liquid sur        | Val    | ues of ai | r pressui<br>/kPa | re in sta | ages |
|-------------------|------|-------------------|--------|-----------|-------------------|-----------|------|
| р                 | туре | m·h <sup>-1</sup> | t<br>1 | t2        | t3                | t4        | t5   |
| S <sub>0(1)</sub> | SS0  |                   |        | -1        | +1                | -1        |      |
| S <sub>1(1)</sub> | SS1  |                   |        | -1        | +1                | -1        |      |
| $S_{0(3)}$        | SS0  |                   |        | -3        | +3                | -3        |      |
| $S_{1(3)}$        | SS1  |                   |        | -3        | +3                | -3        |      |
| $S_{0(5)}$        | SS0  | 0.1               | 0      | -5        | +5                | -5        | 0    |
| S1(5)             | SS1  | 0.1               | 0      | -5        | +5                | -5        | 0    |
| $S_{0(7)}$        | SS0  |                   |        | -7        | +7                | -7        |      |
| $S_{1(7)}$        | SS1  |                   |        | -7        | +7                | -7        |      |
| $S_{0(9)}$        | SS0  |                   |        | -9        | +9                | -9        |      |
| S <sub>1(9)</sub> | SS1  |                   |        | -9        | +9                | -9        |      |

2.3.2 Liquid-liquid mass transfer experiments in c apillary structures of the mixture of kitchen waste a nd straw under the condition of leaching synergistic air pressure fluctuations: Take the mixture of kitchen waste and straw, add sodium chloride after mixing eve nly to get the real material, with chloride ion as an indic ator. There is no gravity water flow out of the real mate rial, so it is considered that chloride ions are distributed in the capillary water of the real material, and the mass transfer efficiency measured under this condition is the liquid-liquid mass transfer efficiency of the capillary str ucture of the real material. Then according to table 2.5 i n order to set the value of air pressure fluctuations for le aching co-pressure fluctuation experiments, with ultra-p ure water as a leaching solution, through peristaltic pu mp for the whole process of water distribution. The exp erimental operation was the same as above.

Table 2.5 Liquid circulation and pressure fluctuation of real material modify the experimental operation parame

|     | •       |  |
|-----|---------|--|
| tor | cetting |  |
| ιci | soume   |  |
|     | 0       |  |

|      |                |      | 0                                  |     |    |    |  |
|------|----------------|------|------------------------------------|-----|----|----|--|
|      | Liquid         | Valu | Values of air pressure in stages / |     |    |    |  |
| Grou | surface        |      |                                    | kPa |    |    |  |
| р    | load∕<br>m∙h⁻¹ | t1   | t2                                 | t3  | t4 | t5 |  |

| S <sub>r(0)</sub>  |     |   | 0   | 0   | 0   |   |
|--------------------|-----|---|-----|-----|-----|---|
| $S_{r(1)}$         |     |   | -1  | +1  | -1  |   |
| $S_{r(3)}$         |     |   | -3  | +3  | -3  |   |
| $S_{r(5)}$         | 0.1 | 0 | -5  | +5  | -5  | 0 |
| $S_{r(7)}$         |     |   | -7  | +7  | -7  |   |
| $S_{r(9)}$         |     |   | -9  | +9  | -9  |   |
| S <sub>r(10)</sub> |     |   | -10 | +10 | -10 |   |
|                    |     |   |     |     |     |   |

#### 2.4 Content and Method of Analysis

The determination of chloride ion refers to the silver nitrate titration method in GB11896-89<sup>[18]</sup>.

The following three indicators were used to verify th e rationality of the model and the reliability of the data. Correlation coefficient,  $R^2$ :

$$R^{2} = \frac{\sum_{i=1}^{n} (\hat{y}_{i} - \bar{y})^{2}}{\sum_{i=1}^{n} (y_{i} - \bar{y})^{2}}$$
(2-1)

Normalized Root Mean Squared Erro, NRMSE:

$$NRSMSE = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}}$$
(2-2)

Nash - Sutcliffe Efficiency, NSE:

$$NSE = 1 - \frac{\sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}$$
(2-3)

 $\hat{y}_i$  is the ith simulated value,  $y_i$  is the ith measured valu e,  $\bar{y}$  is the average of n measured values. The closer the R<sup>2</sup> and NSE are to 1 and the closer the NRMSE is to 0, the better the model performance.

#### 3. Results and Analysis

## 3.1 Derivation of theoretical formula for liquid-liqui d mass transfer in capillary structure enhanced by le aching synergetic air pressure fluctuations based on simple model

The modle is based on the following assumptions: (1) The liquid inside and outside the capillary is an incomp ressible Newtonian fluid. (2) The liquid inside the capill ary is laminar and flow is stable during leaching and the fluctuation of gas pressure. (3) The pore size, number a nd initial capillary water content of the capillaries at an y position in the stacking system are equal. (4) both end s of the capillary tube are filled with capillary water and a small section of the middle of the capillary tube is lef t with a small section of the gas which is an ideal gas. (5) When the external solution enters the capillary tube, it will be mixed with the original capillary water inside the tube instantly.

In the simple model, the total amount of capillary is

*N*, the volume of single capillary is  $V_t$ , the capillary wat er filling rate is  $\varepsilon$ , and the initial concentration of indica tor is  $c_0$ . The volume of the gas column in the tube is  $V_{g0}$  (i.e.,  $V_{g0}=\varepsilon V_t$ ), its initial pressure and the external atmospheric pressure are both  $p_0$ , the pressure fluctuati on is  $\Delta p$ . During a complete air pressure fluctuation cy cle of "atmospheric pressure-negative pressure-positive pressure-negative pressure-atmospheric pressure", the r eplacement of solution inside and outside the capillary s tructure is as follows.

The first is "atmospheric pressure - negative pressure" switching stage. When the external air pressure is switc hed to negative pressure, the air column pressure in the capillary structure is higher than the external air pressur e, so the pressure difference pushes the capillary water out, at the same time, the increase in the volume of the gas column in the capillary tube reduces the pressure. When the column pressure drops to the same as the neg ative pressure external, the pressure difference disappea rs so the capillary water stops discharging, so that the st age of equilibrium is reached. According to Formula 3-1, the amount of capillary water discharged (Formula 3-3) and the mass transfer of solute (Formula 3-4) can be calculated

$$p_0 V_0 = p_a V_a \tag{3-1}$$

 $p_0$  is the pressure of the gas column in the capillary tube at atmospheric pressure, 101.3 kPa;  $V_0$  is the volume o f the capillary tube at atmospheric pressure, 1.9625 mm <sup>3</sup>;  $p_a$  is the pressure of the air column in the capillary tu be after applying pressure difference and rebalancing, 1 02.3 kPa;  $V_a$  is the volume of the gas column in the capi llary tube after applying pressure difference and rebalancing.

$$p_{0}V_{g0} = (p_{0} - \Delta p) V_{g1} \qquad (3-2)$$
$$\Delta V_{l1} = V_{g1} - V_{g0} =$$
$$\frac{\Delta p V_{g0}}{p_{0} - \Delta p} \qquad (3-3)$$
$$m_{l1} = c_{0}\Delta V_{l1} = \frac{\Delta p V_{g0} c_{0}}{p_{0} - \Delta p} \qquad (3-4)$$

The second is "Negative pressure - Positive pressure" switching stage. The situation is reversed from the first stage, the pressure difference pushes the solution outsi de the capillary structure into the capillary structure unt il equilibrium is reached. According to Formula 3-3, th e amount of solution (Formula 3-6) and the concentrati on of indicator (Formula 3-7) can be calculated.

$$(p_0 - \Delta p) V_{g1} = (p_0 + \Delta p) V_{g2}$$
 (3-5)

$$\Delta V_{l2} = V_{g1} - V_{g2} = \frac{2p_0 \Delta p}{p_0^2 - \Delta p^2} V_0$$
(3-6)

$$c_{l2} = \frac{V_t - \frac{p_0}{p_0 - \Delta p} V_{g0}}{V_t + \frac{p_0}{p_0 + \Delta p} V_{g0}}$$
(3-7)

The third is "Positive pressure - Negative pressure" s witching stage. The basic situation is the same as the fir st stage. According to Formula 3-3, the amount of capill ary water discharged (Formula 3-8) and the mass transf er of solute (Formula 3-9) can be calculated.

$$\Delta V_{l3} = V_{g1} - V_{g2} = \frac{2p_0 \Delta p}{p_0^2 - \Delta p^2} V_{g0}$$
(3-8)

$$m_{l3} = c_{l2} \Delta V_{l3} = \frac{2p_0 \Delta p}{p_0^2 - \Delta p^2} \frac{\varepsilon p_0 - \Delta p}{\varepsilon p_0 + \Delta p} V_{g0} c_0 \qquad (3-9)$$

 $V_{g1}$  and  $V_{g2}$  are the volume of the gas column within th e capillary structure at equilibrium in the first and secon d stage respectively, mm<sup>3</sup>;  $\Delta V_{l1}$  is the volume of capilla ry water discharged at equilibrium in the first stage, m m<sup>3</sup>;  $\Delta V_{l2}$  is the volume of solution entered at equilibriu m in the second stage, mm<sup>3</sup>;  $\Delta V_{l3}$  is the volume of capil lary water discharged at equilibrium in the third stage, mm<sup>3</sup>;  $m_{l1}$  is the amount of solute discharged at equilibri um in the first stage;  $c_{l2}$  is the concentration of solute in capillary water after equilibration in the second sta ge, g/mm<sup>3</sup>;  $m_{l3}$  is the amount of solute discharged at eq uilibrium in the third stage, g.

To sum up, in a complete cycle of air pressure fluctua tion, the amount of solute mass transfer  $(m_{ll})$  in a single capillary is shown in Formula 3-10, and the correspondi ng theoretical model of enhanced efficiency  $(\Delta \eta)$  of liq uid-liquid mass transfer is shown in Formula 3-11.

$$m_{lt} = m_{l1} + m_{l3} = \frac{\Delta p}{p_0 - \Delta p} V_{g0} c_0 + \frac{2p_0 \Delta p}{(p_0 - \Delta p)^2} \frac{\varepsilon p_0 - \Delta p}{\varepsilon p_0 + \Delta p} V_{g0} c_0 =$$

$$\frac{\Delta p(p_0 - \Delta p)(\varepsilon p_0 + \Delta p) + 2p_0 \Delta p(\varepsilon p_0 - \Delta p)}{(p_0 - \Delta p)^2 (\varepsilon p_0 + \Delta p)} V_{g0} c_0 \qquad (3-10)$$

$$\Delta \eta = \frac{m_{lt}}{m_{l0}} = \frac{\frac{\Delta p(p_0 - \Delta p)(\varepsilon p_0 + \Delta p) + 2p_0 \Delta p(\varepsilon p_0 - \Delta p)}{(p_0 - \Delta p)^2 (\varepsilon p_0 + \Delta p)} V_{g0} c_0}{\frac{\varepsilon}{1 - \varepsilon} V_{g0} c_0} =$$

$$\frac{[\Delta p(p_0 - \Delta p)(\varepsilon p_0 + \Delta p) + 2p_0 \Delta p(\varepsilon p_0 - \Delta p)]}{\varepsilon(p_0 - \Delta p)^2(\varepsilon p_0 + \Delta p)} (\Delta p \le \varepsilon p_0)$$
(3-11)

The leaching synergetic air pressure experiment of a simple model was carried out under different fluctuatin g pressure values, the capillary water filling rate  $\varepsilon$  in ea ch group of stainless steel capillary tubes was measured after the stainless steel capillary tubes were fully imme rsed, the average of the capillary filling rate  $\varepsilon$  is 42.6%. The theoretical model of liquid-liquid mass transfer efficiency for the simple model (Formula 3-12) is obtained by substituting formula 3-11 under the capillary filling r ate above. The theoretical mass transfer enhancement efficiency can be obtained by taking the corresponding air pressure fluctuation values into account.

 $\eta = \frac{\frac{0.574[\Delta p(p_0 - \Delta p)(0.426p_0 + \Delta p) + 2p_0\Delta p(0.426p_0 - \Delta p)]}{0.426(p_0 - \Delta p)^2(0.426p_0 + \Delta p)}}{(\Delta p \le 0.426p_0)(3-12)}$ 

Taking the atmospheric pressure group as the control group, the difference between the mass transfer efficien cy of each experimental group and the control group is t he real mass transfer enhancement efficiency. As can be seen from Fig. 3.1, the theoretical mass transfer enhanc ement efficiency is higher than the real value at the sam e pressure fluctuation value, because there are some ine vitable errors in the actual capillary packing system, suc h as the fluctuation of capillary filling rate and the unifo rmity of water distribution. Therefore, the theoretical m odel needs to be corrected by stack structure coefficient s. Fig. 3.1 shows that the theoretical value of mass trans fer enhancement efficiency is proportional to the real va lue, which accords with the relation shown in Formula 3-13. The modified coefficient  $(k_s)$  of the stack structur e is 0.425 (R<sup>2</sup>=0.986) by fitting the experimental data in to formula 3-10. The modified semi-theoretical and sem i-empirical model of liquid-liquid mass transfer enhanc ement efficiency can be applied to the simple model as shown in Formula 3-14.



Figure 3.1 The effect of pressure fluctuations on the efficiency of mass transfer enhancement in capillary

$$structures$$

$$\eta_{s} = k_{s}\eta_{m} = k_{s} \frac{0.574[\Delta p(p_{0} - \Delta p)(0.426p_{0} + \Delta p) + 2p_{0}\Delta p(0.426p_{0} - \Delta p)]}{0.426(p_{0} - \Delta p)^{2}(0.426p_{0} + \Delta p)} (3-13)$$

$$\eta_{s} = \frac{0.573[\Delta p(p_{0} - \Delta p)(0.426p_{0} + \Delta p) + 2p_{0}\Delta p(0.426p_{0} - \Delta p)]}{0.426(p_{0} - \Delta p)^{2}(0.426p_{0} - \Delta p)} (\Delta p \le 0.426p_{0}) \quad (3-14)$$

 $\eta_s$  is the enhanced mass transfer efficiency under a simp le model for stainless steel capillary tubes;  $\eta_m$  is the the enhanced mass transfer efficiency calculated by the the oretical model.

In order to verify the applicability and reliability of t he modified semi-theoretical and semi-empirical model, a verification experiment was carried out according to t he operational parameters in table 2.5. The theoretical v alues of mass transfer enhancement efficiency calculate d by formula 3-14 were on a correlation scatter plot and analysed for residuals. The theoretical values of the en hanced liquid-liquid mass transfer efficiency of the capi llary structure in Fig. 3.2 are in the vicinity of the straig htline y=x, indicating that the difference between the th eoretical and experimental values is small.





The residual analysis results of the experimental and theoretical values of mass transfer enhancement efficie ncy are shown in table 3.1. It is shown that the modifie d simple semi-theoretical and semi-empirical model has higher accuracy through the verification experiment an d residual analysis.

Table 3.1 Residual error of fitting value and experiment al value of capillary evaporation flux of simple model o

| 0 | 1    | C      |
|---|------|--------|
| t | aged | refuse |

| υ                            |        |  |  |  |  |
|------------------------------|--------|--|--|--|--|
| Results of residual analysis |        |  |  |  |  |
| R <sup>2</sup>               | 0.9810 |  |  |  |  |
| SRMSE                        | 0.0468 |  |  |  |  |
| NSES                         | 0.9810 |  |  |  |  |

3.2 Modification and application of semi-theoretical and semi-empirical model of liquid-liquid mass tran sfer efficiency in capillary structures enhanced by le aching synergetic air pressure fluctuation based on r eal materials

The real material stacking system differs from the si mple model in capillary water filling rate and capillary structure, which may affect the liquid-liquid mass transf er efficiency of the capillary structure of the real materi al. The volume difference mainly includes the pore volu me and the capillary water filling rate, and the structure difference includes pore structure, strength and the spati al distribution. These two differences between the real materials with the same composition in the theory are r elatively small, so volume correction factor  $k_l$  and struc ture correction factor  $k_2$  are introduced respectively. Th e volume correction factor  $k_l$  corrects for the capillary f illing rate  $\varepsilon$  (Formula 3-15), and the structure correction factor  $k_2$  corrects for the mass transfer enhancement eff iciency (Formula 3-16) corrected by the volume correct ion factor  $k_l$ . a semi-theoretical and semi-empirical mo del (Formula 3-17) for liquid-liquid mass transfer enha ncement efficiency of real materials can be obtained by substituting formula 3-15 and formula 3-16 into formul a 3-12 respectively.

$$\varepsilon_r = k_1 \varepsilon_s \tag{3-15}$$

$$\eta_r = k_2 \eta_s' \tag{3-16}$$

$$\eta_r = \frac{(1-0.426k_1)[\Delta p(p_0 - \Delta p)(0.426k_1p_0 + \Delta p) + 2p_0\Delta p(0.426k_1p_0 - \Delta p)]}{k_1(p_0 - \Delta p)^2(0.426k_1p_0 + \Delta p)} \ \left(3-17\right)$$

 $\varepsilon_r$  and  $\varepsilon_s$  are the capillary water filling rate in the real m aterial stacking system and the simple model of stainle ss steel capillary tube respectively, %;  $\eta_r$  and  $\eta_s$ ' are the mass transfer enhancement efficiency of the model of t he real material stacking system and the simple model o f stainless steel capillary tube corrected by  $k_1$  respectiv ely, %;  $\Delta p$  is the value of air pressure fluctuation, kPa,  $(\Delta p \le 0.426p_0)$ .

The experimental results of liquid-liquid mass transfe r enhancement by leaching and pressure fluctuation are shown in Figure 3.3. Through fitting the above model (Formula 3-17), the volume correction factor  $k_1$  is 0.71 and the structure correction is factor  $k_2$  is 0.22 (R<sup>2</sup> is 0. 9312). Compared with the simple model, the real materi al stacking system is more complex, which results in th e error between the experimental results and the fitting r esults, but it is still greater than 0.9. The experimental r esults show that the difference on the capillary filling ra te and the capillary structure of the same batch is small, and the consistency of the same batch is high. Therefor e, it is feasible to obtain the model of the mass transfer efficiency of real materials by volume correction factor  $k_1$  and structural correction factor  $k_2$ . The semi-theoreti cal and semi-empirical model for enhancing the efficien cy of liquid-liquid mass transfer for real materials is sh own in Formula 3-18.



Figure. 3.3 Experimental results and fitting diagram of actual material liquid circulation synergistic pressure fluctuation enhanced mass transfer  $\eta_r = \frac{0.511[\Delta p(p_0 - \Delta p)(0.3p_0 + \Delta p) + 2p_0 \Delta p(0.3p_0 - \Delta p)]}{(p_0 - \Delta p)^2(0.3p_0 + \Delta p)} (\Delta p \le 30.3 \ kPa)$ (3-18)

This model is applicable to the theoretical analysis of the enhanced efficiency of real material mass tran sfer under the range of  $\pm 0-30$  kPa air pressure fluctu ation (Fig. 3.3). With the increase of air pressure flu ctuation, the enhancement efficiency of mass transfer approaches to 22%, doubled the efficiency of mass t ransfer enhancement compared to the  $\pm 10$ kPa in the above experiments. However, in the practical engine ering application, not only need to consider the techn ical effect, but also need to consider the economics o f the technology. The energy efficiency ratio is introd uced as an economic index, the higher the energy effi ciency ratio is, the more economic it is. The power of two brands of commercially available fans is used as an example. As shown in Figure 3.4, the highest and the second highest energy-efficiency ratio of fan A a nd fan B occurs respectively when the pressure fluct uation is  $\pm 4$  kPa and  $\pm 10$  kPa, the corresponding mas s transfer enhancement is 5.46% and 11.88%, and the fan power is 0.22 kW and 0.48-0.55 kW. The mass tr ansfer enhancement efficiency is improved obviously. Therefore, considering the mass transfer enhanceme nt effect and the energy efficiency ratio, it was deter mined that ±10 kPa was chosen as the air pressure w ave parameter for the subsequent dry anaerobic expe riments.



Figure. 3.4 Theoretical mass transfer enhancement effic iency and energy efficiency ratio under different pressure fluctuations in actual material stackin g systems

#### 4. Conclusion

Using the stainless steel capillary tube as a simple m odel, a semi-theoretical and semi-empirical model of th e liquid-liquid mass transfer enhancement efficiency of the capillary structure of the simple model was obtained by formula derivation and correction of the experiment s on the air pressure fluctuation synergistic leaching. Fu rthermore, using the mixture of food waste and straw as the real material, a semi-theoretical and semi-empirical model of liquid-liquid mass transfer enhancement effic iency in capillary structure applicable to real materials i s obtained was obtained by modifying the simple model. The energy efficiency ratio under each air pressure fluc tuation condition was introduced in the technology appl ication to determine the air pressure fluctuation range, which is  $\pm 10$  kPa, and is used as the process parameter for subsequent dry anaerobic experiments. Experimenta lly, under the air pressure fluctuation value above, the mass transfer efficiency of real material enhanced by le aching and pressure fluctuation was 11.88%.

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### **PROGRESS IN PHOTOCATALYTIC TREATMENT OF LANDFILL**

### **LEACHATE**

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Abstract: Photocatalytic technology is a new technology that uses light energy to catalyze materials. Photocatalytic oxidation technology is an emerging technology in the advanced oxidation method, which is more oxidizing than photochemical oxidation in treating pollutants and is characterized by low cost, non-toxicity, harmlessness and good treatment effect. Garbage leachate is the sewage containing pollutants produced by physical or chemical reaction of garbage in the process of landfill. Using composite photocatalytic materials for deep treatment of landfill leachate, the study utilizes photocatalytic technology in the field of deep treatment of landfill leachate to show the good application prospects and current research progress, and finally puts forward suggestions and prospects for the practical application of photocatalytic treatment of leachate technology.

Keywords: photocatalytic materials, landfill leachate, titanium dioxide

#### INTRODUCTION

With the progress of society, people's lives are getting better and better, and the total amount of urban garbage is increasing year by year. Currently, the main treatment of garbage in China is sanitary landfill, in the process of landfill due to rainfall, compaction and microbial decomposition, the garbage layer will leach a amount of high-concentration certain organic wastewater, that is, garbage leachate<sup>[1]</sup>. With the in-depth research in the field of water treatment, researchers have found that photocatalytic technology has the characteristics of green, does not produce secondary pollution, and the reaction conditions are mild, which is a new technology that can effectively degrade landfill leachate, and it has a broad application prospect in solving environmental problems and energy conversion. Among them, the photocatalytic oxidation technology utilizes the characteristics of good treatment effect and low treatment cost of photocatalyst, and has been more and more widely researched in recent years in the area of landfill leachate.

#### **Characteristics of landfill leachate**

Refuse leachate is a highly concentrated organic wastewater with a complex composition containing a large number of toxic and hazardous substances, such as heavy metals, organic matter, ammonia and nitrogen. The characteristics of landfill leachate mainly depend on the composition and biochemical reactions of the waste pile, local climate, hydrogeological conditions, and the size and age of the landfill site<sup>[3-4]</sup>. Organic wastewater has a high mobility and diffusion and migration capacity<sup>[5]</sup>. If landfill leachate is discharged directly into the environment without effective treatment, it can cause problems such as low oxygen in the water, deterioration of the water quality, and eutrophication, and contamination of the groundwater and the soil, thus seriously threatening human health and the environment. The loss of its utilization value will seriously threaten human health and ecosystems, thus making sanitary

landfills lose their application value<sup>[6-7]</sup>. In order to prevent landfill leachate from polluting the environment, developed countries have put forward extremely strict technical requirements for landfills. In 2008, China promulgated the newly revised GB 16889-2008 "Pollution Control Standards for Domestic Waste Landfills", which put forward more stringent emission standards<sup>[8]</sup>.

#### Hazards of landfill leachate

The hazards of garbage leachate are mainly manifested in the following aspects:1. Water pollution: garbage leachate contains high content of organic matter and heavy metals and other pollutants, which will lead to the deterioration of the quality of the water body, and produce toxic effects on aquatic organisms, and will also affect human health.2. Soil pollution: garbage leachate will change the physicochemical properties of the soil and destroy the structure and fertility of the soil, which will lead to the serious contamination of the soil.3. Environmental health problems: the foul-smelling gas and germs and other pollutants contained in the garbage leachate will pollute the surrounding environment, and at the same time cause environmental health problems, affecting people's normal life.4. Ecological problems: the garbage leachate will be diffused to the surrounding areas through surface runoff, groundwater, etc., which will have an impact on the surrounding ecology and destroy the ecological balance. For the treatment and disposal of garbage leachate, scientific and reasonable measures should be taken to strengthen the control and management of its generation and discharge, so as to reduce its harm to the environment and human beings.

# Development history and significance of photocatalytic technology

The development of photocatalytic technology can be traced back to 1967, when it was discovered that titanium dioxide electrodes could decompose water into hydrogen and oxygen under ultraviolet light irradiation, i.e. the "Hondo-Fujishima effect". This discovery opened a new era of multiphase photocatalysis. In the following decades, photocatalytic technology has been widely researched and applied.

The development of photocatalytic technology is of great significance in solving environmental problems, energy problems and synthesizing organic compounds. Firstly, photocatalytic technology is a green technology that can effectively degrade various dyes, pesticides, heavy metal ions and other pollutants, providing a new way to solve environmental problems. Secondly, photocatalytic technology can also decompose water into hydrogen and oxygen, providing a new method for the manufacture of renewable energy. In addition, photocatalytic technology has a wide range of applications in organic synthesis, such as the oxidation of alcohols, amines, olefins and alkanes or the hydroxylation reaction of aromatic compounds. The development of photocatalytic technology is of great significance in promoting scientific and technological progress, solving environmental problems and promoting human development.

## Overview of the purpose and content of the dissertation research

With the acceleration of urbanization, the problem of landfill leachate is becoming more and more serious. As an emerging environmentally friendly technology, photocatalytic technology has significant advantages in the treatment of landfill leachate. The aim of this thesis is to systematize the research progress of photocatalytic technology in treating landfill leachate, and to explore its application potentials and challenges.

Introduction: to introduce the characteristics and hazards of landfill leachate sources, the principles, characteristics and development history of photocatalytic technology, and to provide basic background knowledge for the subsequent chapters. To summarize the application of photocatalytic technology in landfill leachate treatment in recent years, and to discuss its problems and solutions in landfill leachate treatment. To summarize the application prospects of photocatalytic technology in landfill leachate treatment, and to put forward corresponding countermeasures and suggestions.

## BASIC THEORY OF PHOTOCATALYTIC TECHNOIOGY

#### **Basic principles of photocatalysis**

Photocatalysis is a technology that utilizes light energy for material transformation, and its basic principle is to use light energy to excite electrons from the valence band to the conduction band, and then under the action of electric field or diffusion, these excited electrons and holes migrate to the surface of semiconductor, and oxidation-reduction reaction occurs with the substances adsorbed on the surface of semiconductor. There are three main steps involved: the first step is the photoexcitation process, in which light energy excites electrons from the valence band to the conduction band; the second step is the migration process of electrons and holes, in which excited electrons and holes migrate to the semiconductor surface under the action of an electric field or diffusion; and the third step is the redox process, which is accelerated by the presence of a semiconductor catalyst that accelerates the photoinduced reaction<sup>[9]</sup>.The semiconductor catalyst is irradiated by light with a photon energy higher than that absorbed by the semiconductor. The semiconductor catalyst is irradiated by light with photon energy higher than the semiconductor's absorption value, charge separation occurs, and the semiconductor's valence band electrons produce interband jumps, i.e., electrons jump from the valence band to the conduction band with negative electrons, and there are holes in the valence band, which form electron-hole pairs9-11. In the semiconductor's suspension, the electron-hole pairs can be separated efficiently and migrate to different positions on the surface of the particles to take part in redox reactions on the surface. Reactions. In the practical application of photocatalytic technology, light sources with specific wavelengths and energies, such as

ultraviolet light and visible light, are usually used to obtain the best light excitation effect. At the same time, it is necessary to choose suitable semiconductor materials, catalysts and reactants, etc., in order to realize efficient and environmentally friendly material transformation.

#### Types and properties of photocatalytic materials

Photocatalytic materials are a class of semiconductor catalyst materials that can undergo photochemical reactions under the action of light. The types and characteristics of photocatalytic materials are very rich, and the common ones are titanium dioxide, zinc oxide, tin oxide, cadmium sulfide and so on. These materials all have high photocatalytic activity and can effectively degrade organic matter and reduce metal ions.

Among them, titanium dioxide is a commonly used photocatalytic material with good stability, non-toxicity, high photocatalytic activity, and dual properties of oxidation and reduction. Under the action of light, it oxidizes difficult-to-degrade organic matter into inorganic matter such as carbon dioxide and water. At the same time, titanium dioxide is also able to reduce metal ions in electroplating wastewater, which is a very promising water treatment method.

In addition, zinc oxide and cadmium sulfide also have high photocatalytic activity and can be used for photocatalytic degradation of organic matter and reduction of metal ions. However, due to their unstable chemical nature, they will be photolysed while photocatalytic, dissolving harmful metal ions and having certain biological toxicity, so they have been seldom used as civil photocatalytic materials in developed countries.

In general, the types and characteristics of photocatalytic materials are very diverse, and different materials can be selected according to different needs. However, the stability, toxicity and cost of the materials need to be considered in practical application.

ANALYSIS OF THE CURRENT STATUS OF

### PHOTOCATALYTIC TECHNOLOGY FOR TREATING LANDFILL LEACHATE

## Current status and development of domestic and international research

Due to the more advantages of photocatalytic technology, more and more domestic and foreign scholars have utilized photocatalytic technology to treat a variety of wastewaters in the last decade. Meeroff<sup>[12]</sup> et al. and Poblete<sup>[10]</sup> et al. used TiO<sub>2</sub>, photocatalytic technology to treat landfill leachate and found that the highest COD removal rate could reach 71% and 57%, respectively. Pan Liuming et al.[13] used ozone-enhanced photocatalytic process for deep treatment of landfill leachate and found that the average COD removal rate was above 60% and the BODs/COD of the effluent increased from the initial 0.05 to 0.23 under the optimal process conditions for 2.0 h. This indicates that ozoneenhanced photocatalytic process can increase the treatment capacity as well as improve the biochemistry of the effluent. Jia Chenzhong et al. [14] investigated the changing characteristics of dissolved organic matter in landfill leachate degradation by photocatalytic oxidation with Uv-TiO, and the results showed that the removal of chromaticity, COD, and DOC in landfill leachate degradation by photocatalytic oxidation with Uv-TiO could reach up to 97%, 72%, and 60%, respectively, under suitable conditions. In the photocatalytic 72h treatment, the organic matter species were reduced, from 72 to 44. Leo Wang et al.<sup>[15]</sup> used a suspended composite semiconductor catalyst, ZnO/TiO, for the treatment of municipal landfill leachate, and the experimental results showed that ZnO/TiO, which was more effective in treating the landfill leachate, could achieve a COD removal rate of about 84%, and could be used as a deep treatment of the landfill leachate.2010, Zhao et al.[16] investigated the effect of photocatalysis and electrolysis on leachate treatment, and the results showed that COD, TOC and ammonia nitrogen could be removed up to 74.1%, 41.6%, and 94.5%, respectively, and the organic matter was effectively converted into small molecules of acids.2009, Abdul et al.<sup>[17]</sup> compared the effects of Fenton, TiO2 photocatalysis, and biological treatment with activated carbon adsorption on the treatment of leachate. activated carbon adsorption on leachate. In 2006, Wiszniowski et al.<sup>[18]</sup> investigated TiO<sub>2</sub> photocatalytic oxidation for the deep treatment of biologically treated landfill leachate, and the results showed that 80% of the residual difficult-to-degrade organics were removed from the biologically treated effluent after 300 min of photocatalytic treatment with UV/TiO2.In 2005, de Morais et al.<sup>[19]</sup> investigated the improvement of the biochemistry of mature landfill leachate by various advanced oxidation techniques as pretreatment methods.

## Current main methods and technical routes of photocatalytic technology for treating landfill leachate

As can be seen from the above information, the current research on photocatalytic oxidation treatment of landfill leachate mainly focuses on: ① research on the treatment of landfill leachate by photocatalytic oxidation technology or its combination with other treatment technologies; ② research on the improvement of the biochemistry of landfill leachate by photocatalytic oxidation as a pre-treatment technology. (iii) Research on the deep treatment of landfill leachate by photocatalytic oxidation is photocatalytic oxidation.

## ANALYSIS OF PROBLEMS AND CAUSES OF LANDFILL LEACHATE TREATMENT BY PHOTOCATALYTIC TECHNOLOGY

# Advantages and disadvantages analysis of existing technology

Photocatalytic technology in the degradation of organic pollutants has many obvious advantages, in practical application there are still the following problems<sup>[21]</sup>: ① photocatalytic quantum efficiency is low (about 4%), it is difficult to deal with a large amount

of high concentration of pollutants in the wastewater; (2) spectral response range is narrow, the utilization of solar energy is low; pollutants in the aqueous environment in the TiO<sub>2</sub> catalytic role in the rapid photodegradation, but due to the wide band gap TiO2, only absorb ultraviolet light or the ultraviolet part of solar light ( $\lambda < 387.5$ nm); ③ photocatalytic oxidation efficiency is affected by waste water color, turbidity and a variety of other factors. However, due to the wide band gap of TiO<sub>2</sub>, it can only absorb ultraviolet light or ultraviolet part of sunlight ( $\lambda < 387.5$  nm); ③ The efficiency of photocatalytic oxidation is affected by the chromaticity, turbidity and other factors of the wastewater, so it is less applied to the direct or separate treatment of the complex system of wastewater; (4)The mechanism of multiphase photocatalytic oxidation reaction is not yet clear; due to the complexity of the decomposition of organic reaction process and the variety of intermediary products, the theoretical study of photocatalytic oxidation Due to the complexity of the organic decomposition reaction process and the variety of intermediate products, the theoretical study of photocatalytic oxidation is still in the exploratory stage; (5) The reaction models used are often empirical formulas or simple first-stage reaction kinetic models, and most of the models are derived from the experimental data under the ideal solution state, which is not in conformity with the actual wastewater treatment conditions, and therefore there is a certain gap between them and the practical application; (6) The photocatalyst is easy to deactivate and difficult to recover; due to the superhydrophilicity of TiO<sub>2</sub>, the reaction by-products or intermediate products will take up more space and space in the process of photocatalyst. Due to the superhydrophilicity of TiO2, during the photocatalytic process, the reaction by-products or intermediate products will occupy the active center of the catalyst surface, which prevents the adsorption of degraded substances on the surface of the catalyst, and thus reduces the activity of the catalyst; the loading and separation and recycling of photocatalysts constrain the practical application of photocatalysts<sup>[20]</sup>.

#### Analysis of the causes of the problem

1. Low utilization of light energy: current photocatalytic technology mainly adopts ultraviolet light as light source, and the content of ultraviolet light in sunlight is only 3%, so the utilization of light energy is low.2. Insufficient catalyst activity: current photocatalytic materials have low reactivity for some organic pollutants, which makes it difficult to realize complete degradation.3. Reaction mechanism is not completely clear: there are some blind spots in the understanding of photocatalytic reaction mechanism and principle, which restricts the further development and optimization of technology.4. Lack of efficient and stable photocatalytic materials: current photocatalytic materials are mostly nanoscale powders or thin films, which are difficult to be prepared and costly. Lack of efficient and stable photocatalytic materials: the current photocatalytic materials are mostly nanoscale powders or films, which are difficult to prepare, costly and less stable, which limits the application of photocatalytic technology in large-scale wastewater treatment projects.

## COUNTERMEASURES AND TECHNOLOGY OUTLOOK

## Research on strategies to enhance photocatalytic effect

1. Advanced oxidation technology. This is an efficient, simple, ideal treatment effect of garbage leachate treatment technology, with a fast reaction speed, easy to control the reaction process, degradation of organic matter, thorough, non-polluting, wide range of water quality, etc., can greatly improve the biochemistry of leachate effluent, reduce leachate toxicity. However, it is generally only suitable for difficult to degrade, small flow, high concentration of organic wastewater. Research and production of low-cost, high-efficiency oxidants is the basis for large-scale industrialization of advanced oxidation technology. Catalysts play a crucial

role in advanced oxidation technology, and in-depth research is needed to find catalysts with good catalytic activity, high stability, wide range of application and low cost. Combining with traditional process is the application direction of advanced oxidation technology in recent years<sup>[23]</sup>.

2. Ozone synergistic photocatalytic oxidation. This technology has a good effect on the degradation of organic matter in the landfill leachate and the improvement of its biochemistry. On the one hand, the COD value decreases with the prolongation of time, on the other hand, the difficult biodegradable substances in the leachate are oxidized into small molecule intermediates which are easily absorbed by organisms, so that the BOD value increases and the biochemistry of the leachate can be improved. In view of the effect of ozone-enhanced photocatalysis on the treatment of leachate, this technology can be used in the pretreatment of leachate to improve its biochemistry, or used in the deep treatment of secondary biological effluent. Compared with conventional physicochemical and other advanced oxidation technologies for the treatment of leachate, ozone-enhanced photocatalysis has its own advantages, and it is feasible to use this technology for the deep treatment of leachate<sup>[24]</sup>.

3. Photocatalytic oxidation method. Treatment of landfill leachate has many advantages with strong organic matter removal ability, as the biological treatment process of the follow-up treatment link is not a good treatment method. The use of ultraviolet light as a radiation light source and nanometer as a photocatalyst, have a better treatment effect<sup>[25]</sup>.

### Type and concentration of catalyst R&D and Application of Novel Photocatalytic Materials

Application of new photocatalytic materials in wastewater treatment: Because photocatalytic technology is characterized by high efficiency and no secondary pollution, new photocatalytic materials are widely used in wastewater treatment. For example, the use of  $TiO_2$  and other photocatalysts can remove organic

matter and heavy metal ions in wastewater, further improving the efficiency of wastewater treatment.

Application of new photocatalytic materials in the field of air purification: the use of photocatalytic reaction can remove harmful gases in the air, such as sulfur dioxide, nitrogen oxides, etc., and has many advantages, such as high efficiency, low cost, and not affected by the season.

Application of new photocatalytic materials in new energy development: the use of photocatalytic technology can convert the energy of ammonia and nitrogen in sewage into hydrogen, which can be used in the field of hydrogen fuel cell and other fields to realize new energy development.

The research and development and application of new photocatalytic materials provide new ideas and solutions for solving environmental problems, and make positive contributions to the promotion of sustainable development and protection of the environment.

#### CONCLUSION

#### Suggestions and perspectives for future research

1. Research and development of new photocatalytic materials: for example, nanomaterials and composite photocatalytic materials with higher catalytic activity and light stability. These new photocatalytic materials will help to improve the efficiency of photocatalytic reaction and reduce the treatment cost.

2. Optimization and improvement of photocatalytic technology: The current photocatalytic technology still has some problems, such as harsh reaction conditions and low degradation efficiency of organic pollutants. In the future, the treatment effect and stability can be improved by optimizing the reaction conditions and improving the photocatalytic technology.

3. Joint application with other technologies: In the future, photocatalytic technology can be jointly applied with other technologies, such as combining with biological technology, electrochemical technology, etc., to form a comprehensive treatment method and further improve the treatment effect of landfill leachate.

4. Expanding treatment scale: At present, photocatalytic technology is mainly used in laboratory and small-scale sewage treatment, but in the future, photocatalytic technology can be applied to large-scale garbage leachate treatment through research and improvement, so as to realize industrialized treatment of garbage leachate.

5. Strengthen the mechanism research: in the future, it is necessary to further study the mechanism and principle of photocatalytic reaction in depth, to understand the reaction mechanism and intermediate products in the reaction process, so as to provide theoretical support for the optimization and improvement of photocatalytic technology.

The research prospect of photocatalytic technology for treating landfill leachate is broad, but it still needs to be explored and improved continuously to realize more efficient, stable and economic treatment effect.

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## SEWAGE SLUDGE WITH INDUSTRIAL SOLID WASTE CO-PROCESSING AND SLUDGE BIOCHAR LYTAG PRODUCTS RESEARCH ON RESOURCE UTILIZATION

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#### ABSTRACT

In this project, sewage sludge and industrial solid wastes such as fly ash and carbide slag with volcanic ash activity are co-processed to achieve sludge harmless and resource utilization of sludge biochar lytag products via a low-carbon process. The basic process is to mix dehydrated sewage sludge (moisture content is less than 80%) with fly ash, carbide slag and cement through a roller mixer in a certain proportion, enter the twin-screw granulator, and squeeze out granules through pressure molding; The particles of the sludge mixture are transported to a low temperature aerobic pyrolysis reactor to achieve aerobic pyrolysis of the particles at a low temperature (350-450 °C) and a short residence time (20-30 min). The biochar particles of the pyrolysis product and their volcanic ash activity will be further stimulated to improve the mechanical strength of the lytag, and the sludge biochar lytag product is finally obtained. The sludge biochar lytag has certain adsorption effects on organic carbon and total phosphorus, and can be widely used in pollution control technologies such as treatment of volatile organic compounds, biological filters and constructed wetlands.

#### **0 INTRODUCTION**

Sludge thermal treatment technology as the current mainstream treatment technology includes coal-fired power plant blending, sludge incineration alone and ceramic blending and other forms of technology, but there are generally large investment in treatment facilities, high treatment costs, high carbon emissions and other issues. Other non-mainstream technologies include sludge landfill, sludge composting, sludge pyrolysis technology, etc. Among them, sludge and domestic waste landfill technology has the advantages of less investment and easy operation, but there is a fatal problem that the high water content of sludge affects the normal work of landfill operation machinery; sludge composting technology can realize maximum material recycling and resource utilization, but it faces the problem that the investment in composting facilities is on the high side, and the addition of composting auxiliaries pushes up the treatment cost, and the sludge heavy metal exceeds the standard. However, sludge composting technology can realize maximum material recycling and resource utilization, but faces the challenges of high investment in composting facilities, high treatment cost of composting auxiliary materials, and the problem of sludge heavy metal exceeding the standard affecting the market of composting products. This project proposes that sludge and fly ash, calcium carbide slag and other industrial solid wastes are blended by pressure molding and granulation, and then low temperature aerobic pyrolysis and wet maintenance to produce biochar pellets of the technological route, the research idea is that sewage sludge and fly ash, calcium carbide slag and other industrial solid wastes are synergistically processed, not only to achieve the goal of "waste for waste", but also reduce the mixing materials, and the water content can be utilized in screws. Water content, screw extrusion technology can be used to achieve pressure molding granulation; sewage low-temperature sludge organic aerobic pyrolysis can significantly reduce the generation of liquid-phase hazardous products, but also synchronized exothermic and thus save energy consumption; and finally the use of the corresponding industrial solid wastes in the aerobic pyrolysis process inspired by the volcanic ash reactivity and wet maintenance methods, to obtain the biochar lytags with appropriate mechanical strength and spatial porous structure of the function of the adsorbent material, on the Carbon-containing organic matter, total phosphorus (TP) have a certain adsorption effect, can be widely used in biofilter, artificial wetland and other water pollution control technology.

## 1 RESEARCH BACKGROUND AND THINKING

#### 1.1 Status and problems of sludge treatment technology

Sludge, as a by-product of sewage treatment, has a high water content (dewatered sludge with a water content of about 80%) and a complex composition, in addition to the dominance of biosolids, it also adsorbs or aggregates a variety of hazardous substances such as heavy metals, organic and difficult to degrade substances, etc. and is accompanied by bad odors and bad smells, which can cause secondary pollution if not handled properly. According to statistics, in 2019 China's sludge production has exceeded 60 million tons (at 80% water content), it is expected that in 2025 China's annual sludge production will exceed 90 million tons<sup>[2]</sup>. For a long time, the sewage treatment industry has the problem of "water but not sludge", and there is still a lot of room for the development of sludge treatment and disposal technology.

Sludge thermal treatment technology as the mainstream sludge treatment technology in China includes drying incineration, power plant blending and pyrolysis technology, etc., while other non-mainstream technologies include sanitary landfill and aerobic composting<sup>[3]</sup>.

Aerobic pyrolysis has been developed to overcome the heat transfer bottleneck in the scale-up process of traditional pyrolysis technology. Compared with traditional pyrolysis under anoxic environment, aerobic pyrolysis promotes the formation of free radicals and reduces the activation energy of the reaction to a certain extent, and at the same time, the reaction between oxygen and organic matter will release all the heat required for the primary decomposition of biomass pyrolysis and subsequent secondary reactions. Aerobic pyrolysis has become a hot research topic at home and abroad for its advantages of reducing energy consumption and improving pyrolysis conversion rate<sup>[4-8]</sup>.

Polin<sup>[1]</sup> et al. proposed that in aerobic pyrolysis of biomass, a pellet medium with better thermal properties is better suited for direct contact heat transfer, but is also more difficult to transport and requires complex auxiliary equipment for circulation and heating. Biomass fuel particles have a large specific surface area, which is conducive to the occurrence of oxidation reactions on the surface and inside the pores. During aerobic pyrolysis, oxygen can diffuse to the surface and inside of the biomass pellets, and oxidative-exothermic reactions occur on the surface of the pellets or inside the pores, and the heat generated is not easy to dissipate and is directly utilized for the pyrolysis heat absorption reaction. Chen<sup>[9]</sup> et al. pointed out that the performance of pellets obtained by oxidative aerobic pyrolysis is comparable to that obtained by inert roasting, and it can be used as a substitute for coal in the industry. Aerobic pyrolysis after biomass pelletization facilitates internal heat transfer and reduces heat loss.

In short, sludge treatment and disposal in urban sewage treatment plants is still a difficult problem plaguing the development of the industry. Thermal treatment technology as the current mainstream treatment technology generally exists in the treatment facility investment, high treatment costs, large carbon emissions and other issues. Other non-mainstream technologies, including sludge landfill, sludge composting, etc., there are also operation and maintenance reliability problems, or high investment and operating costs and sludge heavy metal exceeding the standard, etc., the research and development of sludge treatment low-carbon harmless and high-value materials recycling of innovative technologies is of great practical significance.

#### **<u>1.2 Current status of research on sludge</u>** <u>biochar</u>

Solmaz Saadat et al. used Mg, Ca, Al, Cu and Fe impregnation to modify sludge biochar to study its adsorption capacity for phosphate, and the results showed that Ca-rich biochar had excellent adsorption efficacy for phosphate removal, with a maximum P adsorption capacity of 153.85 mg/g<sup>[10]</sup>. Tang et al. used acid and alkali to modify sludge biochar to study its adsorption capacity for the antibiotic Tang et al. used acid-base modified sludge biochar to study the adsorption capacity of tetracycline, and the results showed that the acid-base modified sludge biochar had high adsorption capacity of tetracycline, with the maximum adsorption capacity reaching 286.913 mg/g<sup>[10]</sup>.

At present, there are fewer studies on aerobic pyrolysis of sludge at home and abroad, but based on the aerobic pyrolysis law of cellulose, hemicellulose and other biomass, it can be inferred that aerobic pyrolysis of sludge is favorable to the precipitation of volatile
components due to the presence of oxygen, and lower pyrolysis temperatures (300~400 °C) and longer retention time are conducive to the formation of biochar, which greatly reduces the generation of bio-oil in the process of pyrolysis, and is conducive to the formation of a stable The lower pyrolysis temperature (300~400 °C) and longer residence time are favorable to the formation of biochar, greatly reducing the production of bio-oil in the pyrolysis process, which is conducive to the formation of stable biochar structure. Meanwhile, the aerobic pyrolysis process will release a large amount of heat, which can greatly reduce the energy consumption of sludge in the aerobic pyrolysis process<sup>[19]</sup>.

# **<u>1.3 Research status of fly ash adsorbent</u>** <u>materials</u>

Fly ash is a powdery solid material obtained from the flue gas collected by the dust removal device after the coal powder is burned at high temperature by the furnace. China's generation of fly ash in recent years are more than 500 million t. In 2021, China's annual output of fly 790 ash reached million t, and the comprehensive utilization rate is about 75%<sup>[13-16]</sup>. The main chemical composition of fly ash is SiO $_2$  , Al O $_{23}$  , Fe O $_{23}$  and a small amount of CaO, MgO, etc.[14-16] . The mineral composition of fly ash mainly consists of aluminosilicate vitrinite, crystalline minerals (quartz, lime, magnetite, hematite, etc.) and unburned carbon particles<sup>[14~17]</sup>. Therefore, fly ash and sludge combined with pyrolysis made of biochar ceramic granule products, the product has both a large specific surface area of biochar, space porous structure, functional groups and adsorption sites rich in features, but also has the phosphorus removal characteristics of the fly ash, while the volcanic ash active material hydration water hard gelatinizing compounds can be made for the particles to provide a better particle strength, expanding its application scenarios.

# **1.4 Research Program**

This project in the lower temperature (350  $\sim$  450 °C) and shorter residence time (20  $\sim$  30 min) conditions, the use of adding fly ash, calcium carbide slag and other industrial solid waste and sludge pressure molding granulation and then aerobic pyrolysis to achieve the harmlessness of sludge carbonization and granular biochar ceramic granule product resources.

Dewatering sewage sludge (water content less than 80%) and fly ash, calcium carbide slag,

cement mixed in a certain proportion, into the twin-screw granulator, through the pressure molding extrusion granulation; sludge mixture particles transported to the low-temperature aerobic pyrolysis reactor, the front part of the use of pyrolysis generated by the high temperature exhaust gas preheating, further reduce the moisture content of the material, preheated particles for further aerobic pyrolysis, aerobic pyrolysis and the thermal process of the heat recycling back to the reactor front to achieve direct heat recovery. The hot tail gas generated from the aerobic pyrolysis process is recycled to the front end of the reactor to realize the direct recovery and utilization of heat. The circulating pyrolysis gas circuit is equipped with an oxygen meter, when the oxygen concentration is lower than 10 %, the circulating gas is discharged and the air is replenished, so as to ensure that the circulating pyrolysis gas can be supplied with an excessive amount of oxygen. The recycled pyrolysis gas is cooled down to less than 60 °C through a heat exchanger and then discharged after treatment in a treatment facility. The pyrolysis product, biochar pellets, is further stimulated by wet curing to increase the volcanic ash activity and water hardening reaction, improve the mechanical strength of the pellets, and finally obtain the biochar pellets.

# 2 SLUDGE AEROBIC PYROLYSIS MECHANISM

# 2.1 Experimental materials and methods

The experimental raw materials of sewage sludge came from the sewage treatment plant of Nanjing Gaoke Environmental Science and Technology Co. Ltd. and the sewage sludge was dewatered by a belt filter press with a water content of 70-75 %.

The experiments were carried out using Thermogravimetric and Mass Spectrometry (TG-Ms) and Differential Scanning Calorimetry (DSC) to study the mass change and heat absorption and excretion of sewage sludge under programmed warming conditions (heating from room temperature to 600°C). Nitrogen and air were used as carriers in the experiments, i.e., to study the pyrolysis pattern of sewage sludge under inert and air conditions, respectively. In order to minimize the secondary reaction, the total flow rate of air and nitrogen was controlled to be 50 mL/min. Thermogravimetry was performed using an alumina crucible to enhance the thermal conductivity of the raw material, and the heating procedure was from ambient temperature at a rate of 20 °C/min to 600 °C. The mass spectrometry analysis was mainly

focused on the small molecular gases with high ion flow intensity (CO,  $\rm CO_2$  ,  $\rm CH_4$  ,  $\rm H_2$  ,  $\rm H_2$  O,  $\rm NH_3$  ).

# 2.2 Sludge pyrolysis material changes and weight loss law

# 2.2.1 TG-DTG curve analysis of sewage sludge pyrolysis under air atmosphere:

The TG-DTG curves of the pyrolysis weight loss of sewage sludge under air atmosphere at a heating rate of 20 °C/min are shown in Figure 2-2-1. The results showed that the aerobic pyrolysis process of sewage sludge could be roughly divided into three stages: the first stage (before 120 °C) was the water precipitation stage, which was mainly the precipitation of free water; the second stage was the warming (120-200 °C) and the carbon thermal decomposition of the organic matter (200-420 °C), and there was only one peak of the pyrolysis reaction, with the DTG peak pyrolysis (maximum conversion rate) corresponding to the temperature of 265 °C, the maximum weight loss rate was 48.3 µg/min, and the weight loss rate remained high in this stage, and the weight loss rate was always greater than 30 µg/min in the main pyrolysis temperature interval (230-370 °C); in the third stage (420-610 °C), under the condition of air atmosphere, the residual small amount of organic matter and reaction intermediates continued to occur at the temperature greater than 420 °C In the third stage (420-610 °C), under the air atmosphere, after the temperature is greater than 420 °C, the small amount of residual organic material and the reaction intermediate products continue to undergo thermal decomposition and biochar condensation reaction, the mass change in this stage is relatively small, and the rate of weight loss continues to decrease, with the rate of weight loss of 7-10 µg/min in the temperature range of 420-460 °C, and the rate of weight loss of 2-6 µg/min in the temperature range of 460-600 °C.

The third stage of organic matter carbon pyrolysis of sewage sludge under air atmosphere, because most of the organic matter carbon in the second stage is volatilized by pyrolysis with light gas, formation of intermediate products or formation of biochar, so the weight loss in this stage is slow, and the pyrolysis of residues or aromatization of biochar will continue to take place as the temperature continues to rise, i.e., the carbonyl group, the C-O bond and the C-H bond and other groups remaining in the pyrolysis product biochar are involved in the Aromatization polycondensation, reforming and other reactions to form the final solid phase product biochar.



Figure 2-2-1 TG-DTG curve of sewage sludge pyrolysis under air atmosphere

Based on the above conclusions, by further extending the pyrolysis residence time, it may be possible to remove 85-90 % of the organic matter carbon of sewage sludge by aerobic pyrolysis under air atmosphere at lower pyrolysis temperatures (350-400 °C) and to form a solid-phase product, biochar.

### 2.2.2 TG-DTG curve analysis of sewage sludge and fly ash and other industrial solid waste mixtures under two atmospheres:

The TG-DTG curves of pyrolysis weight loss of sewage sludge mixtures under air atmosphere at a heating rate of 20 °C/min are shown in Figure 2-2-2. The results showed that the addition of industrial solid waste such as fly ash had no obvious effect on the pyrolysis of sewage sludge, and the pyrolysis pattern under two atmospheres of organic matter carbon was consistent with the above pattern.



Figure 2-2-2 TG-DTG curve of sewage sludge pyrolysis under air atmosphere

# 2.3 Heat absorption and excretion law of sludge pyrolysis reaction

The DSC calorimetric curve of the pyrolysis of sewage sludge under air atmosphere is shown in Figure 2-3-1, the heating rate is 20 °C/min, the carrier gas is nitrogen, and the gas flow rate is 50 ml/min. The results show that the DSC curve has a better correspondence with the TG-DTG curve, and the heat-absorption peak around 100 °C corresponds to the precipitation of the free water, and the heat-absorption of the material for the drying of the material. 355 °C corresponds to the exothermic peak of the organic matter carbon of the sewage sludge. 355 °C corresponds to the exothermic peak of sewage sludge organic carbon, due to the delay in the DSC heat measurement, the corresponding temperature is slightly backward compared with the peak of pyrolysis reaction. From the integration of DSC graph, it can be seen that the exothermic amount of aerobic pyrolysis reaction of sewage sludge under air atmosphere is 410.4 J/g, which is converted to 2931 J/g of sewage sludge organic carbon.



Figure 2-3-1 DSC Curve for Pyrolysis of Sewage Sludge in Air Atmosphere

## 3 RESEARCH ON EQUIPMENT AND PROCESS FOR SYNERGISTIC PREPARATION OF BIOCHAR LYTAGS FROM SLUDGE AND FLY ASH AND OTHER INDUSTRIAL WASTES

## 3.1 Mixture granulation system

#### (1) Selection of granulation method

At present, the commonly used pelletizing ceramic pelletizing disc pelletizing, twin-screw extrusion pelletizing and roller extrusion pelletizing, pre-pelletizing various ceramic pelletizing pelletizing methods pelletizing effect of comparison and trial experiments, the final pelletizing system using twin-screw pelletizing machine, through the mandatory way to make the mixture of basic particles of the material bonded to each other, increase, form a certain shape, a certain strength and particle size uniformity, concentration of the wet particles, the machine of the mixture of material The requirements of the machine for the mixture of materials and a certain degree of humidity, so the material mixing and stirring system for the production of the mixture of materials to reduce the humidity of the requirements need not be too strict.

#### 3.2 Aerobic pyrolysis systems

#### (1) Overview of the rotary reactor

This rotary reactor is used for preheating and pyrolysis treatment of mixed pellets of sludge industrial solid waste extruded by twin-screw extrusion The reactor is mainly divided into preheating and pyrolysis sections and is equipped with feeding and air intake systems, discharge and exhaust systems, hot exhaust gas heat exchange system, electric hot plate heating system and integrated support structure.

(2) Material property parameters

The mixture of sludge and industrial solid waste (fly ash: quicklime: phosphogypsum = 7:1:1) in the ratio of 1:1, while adding 3-5 % of waste plastics, through the twin-screw extrusion molding into a pyrolysis rotary reactor. The mass flow rate q of the material entering the reactor is 1 t/h, the water content is 37.5 %, the initial temperature is 25 °C, the density  $\rho$  of the material is 2,000 kg/m<sup>3</sup>, the bulk weight  $\gamma$  is 2 t/m<sup>3</sup>, the natural stack angle a is 45°, the average specific heat capacity is 0.89 KJ/m, and the average specific heat capacity is 0.89 KJ/m.C<sub>s</sub> The average specific heat capacity is 0.89 KJ/(Kg-K).

#### **3.3 Conservation systems**

After the instantaneous combustion stage of the finished particles, with a certain mechanical strength, need to be humidified and constant temperature maintenance, the pilot phase in the laboratory using a constant temperature incubator for maintenance, based on the maintenance conditions to choose the maintenance time, to further improve the mechanical strength of the particles to meet the use of commercial ceramic granule standards.

# 4 CHARACTERIZATION OF BIOCHAR LYTAGS

The application process of biochar ceramic products need to refer to the "artificial ceramic filter media for water treatment" (CJ/T 299-2008) in the ceramic filter media quality requirements, while its COD, TN, TP, NH<sub>4</sub><sup>+</sup>, pH, heavy metal leaching toxicity indicators should be in line with the "urban wastewater treatment plant pollutant discharge standards" (GB18918-2002) limit values.

## **4.1 Concentration of leachate from biochar** <u>lytags</u>

Table 4-1-1 biochar lytags basic water quality index leaching concentration

| norm                   | TN<br>(mg/<br>L) | TP<br>(mg/<br>L) | NH4 <sup>+</sup><br>(mg/<br>L) | COD(m<br>g/L) | p<br>H  |
|------------------------|------------------|------------------|--------------------------------|---------------|---------|
| numer<br>ical<br>value | 2~5              | 0.07~<br>0.15    | 0~0.0<br>8                     | 20            | 7~<br>9 |

| Table 4-1-2 Leaching concentrations of 13 |
|---|
| heavy metals from biochar lytags          |

| norm                   | Cd       | Cu       | As       | Ni       | Zn       | Pb       | Ag       |
|------------------------|----------|----------|----------|----------|----------|----------|----------|
| numer<br>ical<br>value | 1.2      | <2.<br>5 | 5.4      | 4.1      | <6.<br>4 | <4.<br>2 | <2.<br>9 |
| norm                   | Be       | Ba       | Se       | Cr       | Hg       | /        | /        |
| numer<br>ical<br>value | <0.<br>7 | 63.<br>8 | 17.<br>0 | 13.<br>2 | <0.<br>2 | /        | /        |

As can be seen from the above table, the leaching concentration of each substance of biochar ceramic granule is far lower than the limit value of "Pollutant Emission Standard for Urban Wastewater Treatment Plants" (GB18918-2002), and there is no environmental risk when it is used as filter media.

# 4.2 Structural Characterization of biochar lytags

### **4.2.1 BET Specific Surface Area:**

| Table 4-1-3 Specific surface area and po | ore |
|--|-----|
| characteristics of biochar lytags        |     |

| Perfor<br>mance<br>indicat<br>ors | BET<br>spec<br>ific<br>surf<br>ace<br>area<br>/<br>(m <sup>2</sup><br>/g) | Aver<br>age<br>pore<br>size<br>/nm | Pore<br>type | Mesop<br>ore<br>pore<br>volume<br>/(cm <sup>3</sup><br>/g) | voi<br>d<br>rati<br>o<br>/% |
|-----------------------------------|---|------------------------------------|--------------|--|-----------------------------|
| biochar                           | 12~   | 10~1                               | meso         | 0.05~0.  | 40~                         |
| lytags                            | 22  | 4                                  | pore         | 07   | 52                          |

The specific surface area and pore characteristics of biochar ceramic particles are shown in Table 4-1-3, the specific surface area of biochar ceramic particles is  $22 \text{ m}^2/\text{g}$ , the pore type is mainly mesoporous, with an average pore diameter of 14 nm, mesoporous pore volume of  $0.07 \text{ cm}^3$  /g, the micropore specific surface area is  $3.7408 \text{ m}^2$  /g, and the void ratio is 40-50 %, the larger specific surface area and mesoporous structure make the biochar ceramic particles have the potential to adsorb a variety of substances, including phosphate and carbonaceous organic pollutants.

#### 4.2.2 SEM-EDS analysis:

The microscopic morphology of the biochar ceramic grains characterized by SEM-EDS is shown in Figures 4-1-4 and 4-1-5.The SEM images show that the biochar ceramic grains are mainly composed of the microbead structure of fly ash, the porous biochar formed by the pyrolysis of the organic matter carbon, and the formation of a large cavity by the volatilization of water, which exhibit the rough and porous structure of the biochar, i.e., the material combines both the dual properties of fly ash and biochar. However, it is still dominated by the microbead structure of fly ash, and with the hydration reaction of fly ash, the formation of water-hard cementitious compounds such as hydrated calcium silicate and hydrated aluminate may block some of the pores.

The EDS spot-scan spectra showed that the main elemental compositions of the biochar

pellets were C, O, Ca, Si, Al and Fe, which were typical elements composed of calcium silicate and aluminate within the biochar and fly ash, in which C (red) was seen to be uniformly distributed in a point-like manner within the biochar pellets, i.e., forming the pore structure of the biochar pellets. Meanwhile, some common elements in sewage sludge, such as Fe, S and Cu, were found in the EDS spectra.



Figure 4-1-4 SEM microscopic morphology of biochar lytags (magnification 5000X)



Figure 4-1-5 Biochar ceramic granule EDS point-scan profiles

# **5 RESEARCH ON THE APPLICATION OF BIOCHAR LYTAGS**

Biochar ceramic particles have the functional adsorption capacity of both biochar and fly ash, with a large specific surface area and mesopore pore structure, specific surface area of 22 m<sup>2</sup> /g, the average pore size of 14 nm, mesopore pore volume of 0.07 cm<sup>3</sup> /g, the void rate of 40-50 %, with the adsorption of phosphate, carbonaceous organic pollutants with the functional characteristics of the maximum theoretical adsorption of phosphorus at 35 °C for

19.43 mg / g. The biological charcoal has certain potential for application in filtration ponds, artificial wetlands, adsorption removal of carbonaceous organic pollutants and enhanced phosphorus removal. The maximum theoretical adsorption capacity of phosphorus was 19.43 mg/g at 35 °C, which has certain application prospects and potentials in the removal of carbonaceous organic pollutants by adsorption in filtration ponds and artificial wetlands, and enhanced phosphorus removal.

# 5.1 Static adsorption study of biochar ceramic granule stockpiled waste leachate

The adsorption performance of biochar ceramic particles on carbonaceous organic matter was characterized by the static adsorption of biochar ceramic particles on the residual waste leachate from the landfill of Dejiang County, Tongren City, with a COD concentration of 450-550 mg/L. The adsorption capacity of biochar ceramic particles on residual waste leachate was measured by the static adsorption experiments of the beaker (with a liquid-to-solid ratio of 10:1, placed in the horizontal shaker and oscillated for 24 h). The adsorption capacity of biochar lytags was measured by static adsorption test (liquid-solid ratio of 10:1). The experimental results showed that the COD concentration of the residual waste leachate decreased from 500 mg/L and 479 mg/L to 396 mg/L and 413 mg/L, respectively, and the adsorption capacity of the biochar pellets on the carbonaceous organic matter of the residual waste leachate was 0.6-1 mg of carbonaceous organic matter/g. The results showed that the adsorption capacity was 0.6-1 mg of COD/g of the residual waste leachate.

# 5.2 Dynamic adsorption study of biochar lytags for waste leachate

Using biochar ceramic particles drip filtration adsorption device to carry out biochar ceramic particles dynamic adsorption of high-concentration garbage leachate carbonaceous organic experiments, biochar ceramic particles filling height of 200 mm, the surface hydraulic load of 1 m<sup>3</sup> /(m<sup>2</sup> -d), the use of fly ash ceramic particles as a comparative experiment, the COD concentration of garbage leachate for the 5200-5300 mg/L, the control of peristaltic pumps to realize the continuous feed, the first period of two hours to determine the inlet and outlet water COD concentration, the decline in adsorption capacity and every four hours to determine the inlet and outlet water COD concentration changes as shown in Figure 4 The COD concentration of inlet and outlet water was measured once every two hours in the early stage, and the COD concentration of inlet and outlet water was measured once every four hours after the adsorption capacity declined, and the COD concentration of inlet and outlet water of biochar ceramic granule dynamic adsorption of high concentration of waste leachate was changed as shown in Figure 4-2-3.

The results show that, in the early stage of the reaction (0-5 h), the adsorption effect of biochar lytags on carbonaceous organic matter of waste leachate is excellent, and the COD concentration of waste leachate is reduced from 5200 mg/L to 2500 mg/L, and the COD retention and adsorption efficiency is as high as 52%. After 5 h of operation, the COD concentration of the effluent rapidly increased to 4000 mg/L. The reduction of COD in the waste leachate by fly ash ceramic granules was similar to that of biochar lytags, but slightly worse than that of biochar lytags, therefore, part of the reduction of COD in the waste leachate by biochar lytags came from adsorption of COD by biochar lytags (which was better than that of fly ash ceramic granules), and part of the reduction mainly came from physical retention effect of biochar lytags.

#### **5.3** Conclusion

#### 5.3.1 Treatment of low concentration wastewater with biochar lytags:

(1) Adsorption treatment of pumping pit wastewater: Biochar pellets have some effect on the treatment of pumping pit wastewater and other low-concentration wastewater, but the adsorption saturation is faster, the treatment capacity is only 150 L/kg, and the spiral feed on the pellet wear and tear is serious, and need to be further demonstrated that it is used in the first and second level of treatment of the stability of the process and the economics of the process.

(2) Drip filtration treatment of wastewater treatment plant two sedimentation tank tail water: biochar lytags on the wastewater plant tail water purification effect is poor, the pre-treatment of water also exists in the leaching of COD exceeds the risk of the need for recycling degradation of the treatment of the wastewater plant in the tertiary treatment process of the effluent of the limited role in the protection.

#### 5.3.2 Treatment of high concentration wastewater with biochar lytags:

Drip filtration treatment of garbage leachate:

pottery grain treatment of garbage leachate decarbonization and phosphorus removal performance is still available, but the garbage leachate water quality is complex, there is the possibility of plugging the holes in the later stage, adsorption performance is reduced, and adsorption of saturated ceramic grain subsequent disposal methods still need to be further discussed.

#### **6 SUMMARY**

#### 6.1 Social benefits

Sludge and fly ash, phosphogypsum and other industrial solid waste synergistic treatment to achieve "waste for waste", while opening up a low-carbon energy, high-value material sludge treatment technology innovation path.

# <u>6.1.1 Low-carbon, non-hazardous and</u> <u>high-value materialized recycled sludge</u> <u>treatment technologies:</u>

technological innovation This has developed a low-carbon harmless and high-value material recycling sludge treatment technology, through low-temperature aerobic pyrolysis technology to achieve the harmlessness of sludge carbonization, while biochar ceramic granule products are used for VOC treatment or biofilter, artificial wetlands to remove difficult to degrade organic matter, adsorption saturation can be returned to the low-temperature aerobic pyrolysis rotating reactor regeneration, regeneration can be reused so as to achieve the high-value material. Recycling of high-value materials.

#### <u>6.1.2 Co-processing of sludge and</u> industrial solid waste:

This technology synergistically treats sludge with fly ash, phosphogypsum and other industrial solid wastes, and also makes the biochar ceramic granule products not only have sufficient mechanical strength, but also have the porous adsorption performance of biochar and the highly efficient phosphorus removal composite function of fly ash-based particles , which realizes the synergistic treatment of sludge and fly ash, phosphogypsum and other industrial solid wastes and their resourceful utilization, and achieves the purpose of "treating wastes with wastes". The purpose is "waste for waste".

# 6.1.3 Carbon reduction:

This technology utilizes aerobic heat release to provide the energy required for pyrolysis and preheat drying, reducing the energy consumption of sludge treatment and thus reducing indirect carbon emissions (carbon emissions from the use of fossil energy), and at the same time realizing the harmlessness of sludge carbonization by means of low-temperature aerobic pyrolysis, i.e., the so-called low-carbon and harmless treatment and resource utilization.

# **6.2 Expected economic benefits**

Compared with the current mainstream sludge thermal treatment technology program, this technology has obvious technical and economic comparative advantages in the technical route, process conditions, operation and management, etc., specifically including: 1) the use of low-temperature aerobic pyrolysis technology, the reaction process exothermic heat can be balanced between the granular material and pyrolysis stage energy demand, energy recycling and utilization is more direct and convenient, so this technology route is a simpler system of energy reuse (hot exhaust gas direct Therefore, the energy reuse system of this technology route is simpler (the hot tail gas is directly recycled), and the energy consumption level is lower; 2) the process is simpler, and the main process equipment, low-temperature aerobic pyrolysis rotary reactor, does not need high-temperature and high-pressure process conditions, so the investment in engineering has an obvious comparative advantage; 3) in terms of operation and management, because of the simplicity of the process, it can realize a more reliable automatic control, and the personnel cost of operation and maintenance management can be effectively reduced.

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# An Ammonium Leaching Process for the Recovery of Heavy Metals from Municipal Solid Waste Incineration Fly Ash

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Keywords: Fly ash, acid leaching, heavy metals, aeration, metallic aluminum.

#### Abstract:

This study presents an ammonium-leaching process for recovering zinc (Zn) and copper (Cu) from municipal solid waste incineration (MSWI) fly ash produced by incineration plants that use dry or semi-dry flue gas treatment methods. The leaching rates for Zn and Cu were 54.39% and 86.23%, respectively, with total recovery rates of 52.21% and 85.28%, respectively. The recovered precipitate contained substantial Zn (33.62%) and Cu (14.19%) concentrations, making it suitable for metal smelting. Additionally, the ammonium leaching process demonstrated effective reduction and dechlorination of the fly ash. The mass of the treated fly ash was reduced to 30.63% of the original, and the chlorine content decreased significantly from 26.23% to 0.84%. The findings of this study support the sustainable utilization of MSWI fly ash by enabling valuable resource recovery and facilitating its potential conversion into construction materials.

#### 1. Introduction

In Japan, incineration is a commonly used method for municipal solid waste (MSW) disposal due to its benefits, which include energy recovery and reduction of MSW mass and volume (Hjelmar 1996). And from 2013 to 2022, the proportion of waste incineration in China rose from 27% to 80%. By 2022, China had 648 operational municipal waste incineration plants, incinerated 195.021 million tons of waste (中国统计年 鉴). However, this process generates both fly ash and bottom ash. MSWI fly ash is considered hazardous waste in numerous countries due to the presence of highly toxic elements, such as Pb, Cd, Cr, Hg, Sb, and As, and trace amounts of persistent organic pollutants (Yuying Zhang et al. 2021; Shunda Lin et al. 2022). To address this issue, various methods for the harmless treatment of MSWI fly ash, such as cement-based stabilization/solidification, thermal treatment, cement clinker co-combustion, etc., have been developed and applied to minimize the environmental impact of MSWI fly ash (Fan, Wang, and Zhang 2018). Nevertheless, it is vital to recognize the limitations of these techniques, as they are unable to achieve the recovery of valuable metals (Zn, Cu, Pb, Sb, and K) from MSWI fly ash (Tang et al. 2022; 2018; 2019).

However, the leaching method is highly effective for recovering heavy metals from fly ash. In Switzerland, more than 60% of municipal solid waste incineration (MSWI) fly ash undergoes acid leaching to recover these metals (Vehlow et al., 1990.; Weibel et al. 2018; Quina et al. 2018). This acid-leaching process, known as FLUWA, utilizes scrubber water from the wet flue gas treatment system as the leaching agent to extract heavy metals from fly ash. However, in Japan and China, most incineration plants employ dry or semi-dry methods for flue gas treatment, which do not generate acidic wastewater. Therefore, this study proposes an ammonium-leaching process as an alternative to recover heavy metals from fly ash in incineration plants using dry or semi-dry methods. As shown in Fig. 1, the proposed process is designed to enhance the recovery of MSWI fly ash. In this process, NH<sub>4</sub>Cl acts as the lixiviant, and its recyclability within the system is maintained through its reaction with calcium ions in the leachate and carbon dioxide in the flue gas, as illustrated by the following reaction:

$$2NH_3 + Ca^{2+} + CO_2 + H_2O \rightleftharpoons 2NH_4^+ + CaCO_3 \downarrow (1).$$

In this study, the ammonium leaching and ammonia removal steps were conducted to achieve the recovery of Zn and Cu form MSWI fly ash. And the specific objectives of this study are to evaluate the Zn and Cu recovery rate of the proposed process, determine the Zn and Cu concentration in the generated precipitate, and characterize the treated fly ash.



Fig. 1 The simplified process flow diagram of the proposed process.

#### Table 1

The chemical composition of Raw FA, Leached FA and Heavy metal precipitate (LOI: Raw FA 6.057 wt.%, Leached FA 7.613 wt.%, Heavy metal precipitate 7.302 wt.%).

| Flomont |        | Concentration | (mg/kg)                 |
|---------|--------|---------------|-------------------------|
| Element | Raw FA | Leached FA    | Heavy metal precipitate |
| Si      | 47372  | 135892        | 2311                    |
| Al      | 9107   | 36650         | 2124                    |
| Fe      | 4840   | 15236         | 210                     |
| Ti      | 2400   | 8197          | 0                       |
| Mn      | 170    | 516           | 65                      |
| Р       | 2460   | 8177          | 285                     |
| Ca      | 253815 | 266046        | 154051                  |
| Mg      | 14970  | 14578         | 7789                    |
| Na      | 57715  | 8935          | 97142                   |
| K       | 30895  | 3384          | 697                     |
| Cl      | 262277 | 8407          | 56773                   |
| S       | 17943  | 40470         | 14057                   |
| F       | 310    | 1477          | 87                      |
| Zn      | 15085  | 22467         | 336179                  |
| Cu      | 3771   | 1515          | 141857                  |
| Pb      | 3805   | 11735         | 312                     |
| Cr      | 130    | 393           | 24                      |
| Ni      | 64     | 147           | 471                     |
| Ba      | 456    | 2352          | 0                       |
| Sb      | 1793   | 6547          | 0                       |
| Sn      | 0      | 0             | 3866                    |
| Sr      | 149    | 307           | 7                       |
| As      | 25     | 78            | 2                       |
| V       | 1      | 4             | 0                       |
| Cd      | 288    | 154           | 7847                    |
| Со      | 4      | 7             | 0                       |

#### 2. Materials and methods

#### 2.1 Materials

The fly ash sample used in this study was collected from a stoker grate incineration plant in F City, Japan. The fly ash sample was initially in a dry state and was stored in an airtight container after collection. In Japan, municipal solid waste is categorized for the purpose of resource recovery and proper disposal. However, the classification methods vary across different regions. In the case of F City, municipal solid waste is sorted into four categories: combustible refuse, non-combustible refuse, glass and PET bottles, and bulky refuse. At this incineration plant, only combustible refuse is used as waste input.



Fig. 2 Fly ash leachate before and after ammonia removal, raw fly ash and heavy metal precipitate recovered: (a) The fly ash leachate after leaching with  $0.6 \text{ mol/l NH}_4\text{Cl}$  for 1 h at room temperature; (b) The fly ash leachate after ammonia removal; (c) Raw FA; (d) Heavy metal precipitate.

# 2.2 Ammonium leaching

The fly ash sample weighing 20 g was placed in a 250 ml air-tight polypropylene bottle. Subsequently, 100 ml of ammonium chloride solution was added to the bottle. The mixture was then sealed and stirred at 400 rpm for a specific duration at room temperature. Following the leaching step, the pH of the mixture was measured. Solid and liquid phases were separated using a 0.45  $\mu$  m

filter membrane. Subsequently, the solid phase was washed two times with 50 ml of deionized water and oven-dried at 105  $^{\circ}$ C for 24 hours. The liquid sample was acidified using nitric acid and stored for subsequent analysis.



**Fig. 3** (a) Effect of the contraception of NH<sub>4</sub>Cl on leaching of Zn, Cu, Pb and Cd under an S/L ratio of 1:5 and room temperature after 1 hour of leaching; (b) Relationship between leachate pH and NH<sub>4</sub>Cl concentration under an S/L ratio of 1:5 and room temperature after 1 hour of leaching; (c) Effect of time on leaching of Zn, Cu under an S/L ratio of 1:5 and room temperature with 0.6M NH<sub>4</sub>Cl.

#### 2.3 Ammonia removal

In this experiment, 250 ml of the separated leachate was transferred to a 500 ml beaker heated to boiling and stirred at 500 rpm. The pH of the leachate was subsequently adjusted to  $9 \pm 0.1$  with the addition of 1mol/l NaOH. The heating process persisted for about 30 minutes after boiling until a substantial quantity of blue precipitates formed, the leachate's pH kept stable. Following the cessation of heating, the mixture separated into solid and liquid phases through centrifugation at a speed of 3000 rpm for 5 minutes. The solid phase was washed twice with 50 ml of deionized water, then oven-dried under 105 °C for 24h. The leachate was filtered with a 0.45  $\mu$  m membrane and adjusted to a final volume of 250ml using deionized water for further analysis.

#### 2.4 Sample characterization

The elemental composition of the initially collected fly ash samples (Raw FA), leached fly ash samples (Leached FA), and heavy metal precipitate were determined by energy dispersive X-ray fluorescence analysis (ED-XRF) using a Spectro Xepos spectrometer with matrix-adjusted calibration. The measurements were performed on pressed powder pellets (32 mm). Qualitative identification of mineral phases of Raw FA, Leached FA and heavy metal precipitate were performed by the X-ray diffraction (XRD) technique. Before the analysis, samples were manually ground to powder with a mortar. Analyses were conducted in a Rigaku Multiflex diffractometer by CuKa radiation under the 2-theta range of 2-75° and scanning step of  $0.02^{\circ}$  at the beam current of 30 mA and the voltage of 44 kV. Jade (v. 9.0) and PDXL (v. 2.1.2.0) software packages were used for the phase identification.

A modified three-step sequential BCR (European Community Bureau of Reference) extraction procedure was employed to elucidate the speciation distributions of heavy metals in the fly ash samples before and after leaching (Gabarrón et al. 2019; Gleyzes, Tellier, and Astruc 2002; Soliman, El Zokm, and Okbah 2018). Due to the high alkaline content in fly ash and considering that the method was initially designed for soil and sediment analysis, an adjustment was made to the first step of the modified BCR extraction in this study (Tong et al. 2020). Specifically, the acetic acid concentration was increased from 0.11M to 0.5M. This modification aimed to ensure the thorough leaching of heavy metals bound to carbonate fractions, accommodating the unique characteristics of fly ash in terms of its alkalinity. The four identified fractions were designated as the exchangeable/carbonate fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4), respectively. Each extraction step involved centrifugation at 3000 rpm for 15 minutes,

followed by filtration of the supernatant liquid through a 0.45  $\mu$  m filter membrane.



**Fig. 4** XRD pattern of fly ash samples and heavy metal precipitate: (a) Raw FA; (b) Leached FA; (c) Heavy metal precipitate.

Moreover, an internal check was conducted to assess the reliability of the sequential extraction method. This involved determining the recovery percentage by comparing the sum of the four fractions (F1, F2, F3, and F4) with the total concentrations of heavy metals obtained through pseudo-total digestion, expressed as:

Recovery rate = 
$$\frac{F_1+F_2+F_3+F_4}{\text{Total concentration}} \times 100 \ (\%)$$
 (2);

Liquid samples were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, 720 ICP-OES, Agilent Technologies), following acid digestion by analytical grade nitric acid (HNO3).

#### 2.5 Simulation

Visual MINTEQ (v 3.1) was used to calculate the concentrations of Zn, Pb, Cu, and Cd in leachate under varying pH conditions at a temperature of 99 °C to identify the optimal pH value for the ammonia removal experiment. The equilibrium speciation model was based on precipitation/dissolution/complexation equilibrium reactions. To simplify the simulation, only the metal cations Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> are considered, along with the anion Cl<sup>-</sup>. The concentrations of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ , and  $K^+$  in the leachate with NH<sub>4</sub>Cl at a concentration of 0.6 mol/l are initially 0.022 mol/l, 0.0087 mol/l, 0.00034 mol/l, 0.73 mol/l, 0.71 mol/l, and 0.23 mol/l, respectively. However, due to the maximum ionic strength limit of 1 in Visual MINTEQ (v 3.1), the concentrations of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ , and  $K^+$  are proportionally reduced to 0.0055 mol/l, 0.0022 mol/l, 0.000085 mol/l, 0.18 mol/l, 0.18 mol/l, and 0.058 mol/l, respectively. The concentration of Cl<sup>-</sup> ions is adjusted to 0.61357 mol/l.

The simulation calculations were performed at 99  $^{\circ}$ C, exploring different pH values to achieve the equilibrium concentrations of  $Zn^{2+},\ Cu^{2+},\ Cd^{2+},\ and$  $Ca^{2+}$ reaching in the solution when the dissolution-precipitation equilibrium. Subsequently, precipitation rates were computed using Formula (3). This simulation aimed to identify the optimal pH for boiling ammonia removal, maximizing ammonia removal efficiency at a sufficiently high pH while ensuring the comprehensive precipitation of heavy metals, particularly calcium, without excessive precipitation.

Precipitation rate = 
$$\frac{\text{Initial concentration} - Equilibrium concentration}{\text{Initial concentration}} \times 100 (\%) (3);$$

Additionally, simulations were conducted to explore the relationship between the chemical speciation of ammonia (NH<sub>4</sub><sup>+</sup>, free NH<sub>3</sub>, and NH<sub>3</sub> complexed with metals) and pH under the conditions where  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $K^+$ , NH<sub>4</sub><sup>+</sup>, and Cl<sup>-</sup> concentrations were

determined to be 0.0055 mol/l, 0.0022 mol/l, 0.00085 mol/l, 0.18 mol/l, 0.18 mol/l, 0.058 mol/l, 0.15 mol/l and 0.76357 at  $25 \,^{\circ}\text{C}$ . These results serve as a foundation for determining the optimal concentration of ammonium chloride.



**Fig. 5**: Simulation Results: (a) Relationship between Precipitation Rate of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ , and  $Ca^{2+}$  with pH at 99 °C; (b) Relationship between the proportion of NH<sub>4</sub><sup>+</sup>, free NH<sub>3</sub>, and complexed NH<sub>3</sub> with pH.

2.6 The determination of alkaline content in MSWI fly ash

Take approximately 0.5g of finely ground fly ash sample and place it in a conical flask with a ground glass stopper, which has a capacity of 250 ml. Add 4g of sucrose and a magnetic stir bar, then pour 40 ml of freshly boiled and cooled deionized water. Seal the flask tightly with the stopper and stir for 25 minutes. Add 2-3 drops of phenolphthalein indicator and titrate with 0.5mol/l hydrochloric acid standard solution until the red color disappears and remains absent for 30 seconds.

#### 2.7 Quality assurance (QA)/quality control (QC)

Each experiment, encompassing ammonium leaching, ammonia removal, XRF analysis, BCR sequential extraction procedure, alkalinity assessment in fly ash, and heavy metal concentration quantification in the liquid phase using ICP-OES, was conducted in triplicate. This threefold repetition was employed to ensure the obtained data's accuracy, reliability, and consistency across diverse analyses and procedures.

#### 3. Results and discussion

3.1 Characterization of the original collected fly ash sample

According to Table 1, the original collected fly ash sample exhibits a high Ca content of 25.38 wt.%. Additionally, from Fig. 4 (a), it can be observed that calcium predominantly exists in the forms of CaClOH, CaCO<sub>3</sub>, and CaSO<sub>4</sub> in the fly ash. Furthermore, the fly ash contains an alkali content of 10.83 wt.% (calculated as Ca(OH)<sub>2</sub>), indicating a significant acid neutralization capacity. Consequently, acid-leaching methods for extracting heavy metals from fly ash would entail substantial acid consumption. However, an alternative approach utilizing ammonium salts for leaching can effectively consume the alkali content in fly ash while generating ammonia that is easy to remove and recycle, potentially reducing the overall treatment cost.

According to Table 1, the content of Zn and Cu in fly ash is 1.58% and 0.36%, respectively. According to the Chinese geological and mineral industry standards, the Zn content in fly ash satisfies the prescribed cut-off grade range of 1.5-2.0% (DZ/T 0214-2020). The material with metal content greater than the cut-off grade is designated as ore because, under the existing economic situation, not only will this material pay for the cost of mining, processing, and refining, but it will also generate some profit (Hagni, Hagni, and Demars 1991; Thompson and Barr 2014; Asad, Qureshi, and Jang 2016).

#### 3.2 Ammonium leaching

The raw fly ash was subjected to leaching with the NH<sub>4</sub>Cl solution at a solid-liquid ratio of 1:5. The alkaline substance in the fly ash, which reacted with NH<sub>4</sub><sup>+</sup>and generated NH<sub>3</sub> that subsequently formed complexes with the Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> ions. This complexation reaction resulted in their leaching out into the leachate. The color of the leachate turned blue, contributed to the formation of Cu(NH<sub>3</sub>)<sup>2+</sup><sub>4</sub>.

| $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$ | (4 | ł) | ); | , |
|--|----|----|----|---|
|--|----|----|----|---|

| $4\mathrm{NH}_3 + \mathrm{Cu}^{2+} \rightleftharpoons$ | $Cu(NH_3)_4^{2+}$ | (5 | ) | ; |
|--|-------------------|----|---|---|
|  |                   |    |   |   |

 $4NH_3 + Zn^{2+} \rightleftharpoons Zn(NH_3)_4^{2+}$ (6);  $4NH_3 + Cd^{2+} \rightleftharpoons Cd(NH_3)_4^{2+}$ (7);

$$2\mathrm{NH}_3 + \mathrm{Ca}^{2+} \rightleftharpoons \mathrm{Ca}(\mathrm{NH}_3)_2^{2+} \tag{8}.$$

As shown in Fig. 3 (a), the concentrations of Zn ,Cu and Cd in the leachate significantly increased with increasing NH<sub>4</sub>Cl concentration. However, the concentration changes were insignificant after the NH4Cl concentration exceeded 0.6 mol/l. In contrast, the concentration of Pb decreased significantly after the NH<sub>4</sub>Cl concentration exceeded 0.4 mol/l, which was attributed to the rapid decrease in pH with increasing NH<sub>4</sub>Cl concentration (as shown in Fig. 3 (b)). Pb is an amphoteric metal, and Pb<sup>2+</sup> can form complexes with hydroxide ions at high pH conditions and be leached out. As the pH decreases, Pb<sup>2+</sup> exists in the form of Pb(OH)<sub>2</sub> precipitate, leading to a significant decrease in leaching concentration (Yan Zhang, Jiang, and Chen 2008).

When using a 0.6 mol/l ammonium chloride solution as the leaching agent, the pH of the leachate is 10.3. According to Fig. 5 (b), it can be inferred that at this point, NH<sub>4</sub><sup>+</sup> constitutes approximately 10% of the total ammonia content, while at a pH of 9.5, NH4<sup>+</sup> constitutes approximately 38.5% of the total ammonia content. Although increasing the concentration of ammonium chloride slightly enhances the leaching concentration of Zn, it significantly increases the proportion of NH4<sup>+</sup>. This would result in a higher alkali consumption during the ammonia removal step. Therefore, a 0.6 mol/l ammonium chloride solution is chosen for leaching fly ash. As shown in Fig. 3 (c), under a solid-liquid ratio of 1:5 and at room temperature, the leaching amounts of Zn and Cu from the fly ash using 0.6 mol/l NH4Cl solution did not significantly increase with time. This indicates that the reaction has reached equilibrium after 1 hour.

After leaching, the mass of fly ash accounts for 30.63% of the original ash mass. The concentrations of Zn and Cu in the leached fly ash are 22,463 mg/kg and 1,516 mg/kg, respectively. Using the following formula, the leaching rates for Zn and Cu can be calculated as 54.39% and 86.23%, respectively.

Leaching rate = 
$$\frac{M_0 \times C_0 - M_1 \times C_1}{M_0 \times C_0} \times 100$$
 (%) (8);

Mo: The mass of the original fly ash sample (g);

Co: The content of a particular metal in the original fly ash sample (mg/kg);

Ml: The mass of leached fly ash sample (g);

Cl: The content of a particular metal in a leached fly ash sample (mg/kg).

## 3.3 Recovery of Zn and Cu

A distillation method was used to remove ammonia from the solution. After the ammonia was removed, the ammonia complexes of Zn, Cu, and Cd were decomposed, and they reacted with hydroxide ions and chloride ions to form precipitates. According to the simulation results, under the conditions of 99  $^{\circ}$ C and pH 9, the precipitates formed at equilibrium include aincite (ZnO, white), tenorite (CuO, black), and cadmium hydroxide (Cd(OH)<sub>2</sub>, white). In Fig. 4 (c), the presence of ZnO is observed, which is consistent with the result of simulation. However, from Fig. 2 (b) and (d), it is evident that the generated precipitate is light blue, suggesting the probable formation of blue Cu(OH)<sub>2</sub> or green Cu<sub>2</sub>(OH)<sub>3</sub>Cl during the ammonia removal process. The absence of a black color is likely because the reaction has not reached equilibrium yet. If given sufficient time, these blue precipitates may eventually turn black. Additionally, during the ammonia removal process, black precipitates were indeed observed on the walls of the beaker. Additionally, the peak of CuCl<sub>2</sub> found in the precipitate is likely the result of the decomposition of Cu<sub>2</sub>(OH)<sub>3</sub>Cl during oven drying. However, the XRD results do not show peaks for Cu(OH)2 and Cu2(OH)3Cl, possibly due to their existence in an amorphous phase.

The removal efficiency of ammonia increases with the increase in pH value and temperature (Krakat et al. 2017). However, the removal of ammonia and the generation of heavy metal hydroxides can cause a decrease in the pH value of the leachate. Therefore, a sodium hydroxide solution was used to maintain the pH of the leachate. However, due to the high concentration of calcium ions in the leachate, a high pH value can cause calcium precipitation, affecting the concentration of heavy metals in the recovered precipitate. Therefore, a simulation was used to determine the pH for ammonia removal.

As shown in Fig. 5 (a), the precipitation of Zn, Cu, Cd, and Ca is closely related to the pH of the leachate. When the pH exceeds 9, the precipitation rates of Zn, Cu, and Cd approach 100%, and calcium begins to precipitate from pH 9.9. A higher pH is favorable for improving the efficiency of ammonia removal. Therefore, in this study, the pH of the leachate was controlled at  $9\pm0.1$  to enhance the recovery efficiency of heavy metals and ammonia removal efficiency while avoiding the precipitation of calcium.

After removing ammonia, the concentrations of Zn and Cu in the leachate are 0.578 mg/l and 0.063 mg/l, respectively. The recovery rates for Zn and Cu from the leachate are 95.99% and 98.90%, respectively. Therefore, the total recovery efficiencies are 52.21% and 85.28% for Zn and Cu, respectively. The contents of Zn and Cu in the recovered heavy metal precipitate are 33.62% and 14.19%, respectively, making the precipitate an excellent material for metal smelting.



**Fig. 6**: (a) Relationship between acetic acid concentration and leachate pH;(b) Relationship between metal concentrations in leachate of Raw FA and acetic acid concentration;(c) Relationship between metal concentrations in leachate of Leached FA and acetic acid concentraction.

3.4 Characterization of fly ash after treatment Based on Fig. 4 (a), the predominant crystal phases in the original ash are NaCl, KCl, CaClOH, CaSO<sub>4</sub>, and CaCO<sub>3</sub>. Fig. 4 (b) shows that the NaCl, KCl, and CaClOH peaks disappear entirely after leaching. NaCl and KCl, being soluble salts, dissolve during the leaching and washing processes. CaClOH reacts with NH<sub>4</sub><sup>+</sup> to form soluble CaCl<sub>2</sub>. Furthermore, according to Table 1, the chlorine content in the leached fly ash decreases significantly from 26.23% to 0.84%. This substantial reduction in Cl content enhances the potential for utilizing the leached fly ash as a construction material or raw material for cement, as high chloride content can cause steel reinforcement corrosion (Balonis et al. 2010; Chen et al. 2012).



**Fig.** 7 Comparison of heavy metal speciation forms in Raw FA and Leached FA.

In addition, this study employs the modified BCR method to analyze the speciation distribution of Zn, Cu, Pb, and Cd in both Raw FA and Leached FA. However, the modified BCR method was initially developed to determine heavy metals' speciation distribution in soils and sediments(Gabarrón et al. 2019; Gleyzes, Tellier, and Astruc 2002; Gabarrón et al. 2019; Soliman, El Zokm, and Okbah 2018). In the first step of the modified BCR, a 0.11 mol/l acetic acid solution is used to leach the samples, aiming to dissolve soluble salts, hydroxides, and carbonates of heavy metals. Nevertheless, fly ash exhibits a much higher acid-neutralizing capacity than soils and sediments. As shown in Fig. 6 (a), when the acetic acid concentration is 0.11 mol/l, the pH of the leachate from both Raw FA and Leached FA is around 6, making it ineffective in decomposing heavy metal carbonates(Tong et al. 2020). As depicted in Fig. 6 (b) and (c), the concentrations of various heavy metals increase with the rise in acetic acid concentration, with a more pronounced increase in the leachate from Leached FA. This might be attributed to a higher proportion of heavy metals in carbonate form in Leached FA, making it more susceptible to the influence of acetic acid concentration. Additionally, it is observed that when the acetic acid concentration increases to 0.5 mol/l and the leachate pH drops to around 4, further increasing the acetic acid

concentration does not significantly affect the metal concentrations in the leachate. Therefore, this study employs 0.5 mol/l acetic acid as the leaching agent for the first step of the modified BCR.

As shown in Fig. 7, compared to Raw FA, the proportion of Zn, Cu, and Cd in the exchange/carbonate fraction of Leached FA significantly decreases. In contrast, the proportions in the reducible, oxidizable, and residual fractions show a noticeable increase. This may be attributed to heavy metals in soluble salt or hydroxide forms leaching out by ammonium chloride, leading to a relatively higher proportion of the other three speciation forms. Although ammonium chloride only leaches a small amount of Pb, the exchange/carbonate and reducible forms of Pb in Leached FA significantly decrease, while the oxidizable and residual forms increase significantly compared to Raw FA.

# 4. Conclusion

In conclusion, the ammonium chloride leaching process has shown promising results for the selective extraction of Zn and Cu from fly ash. By employing a solid-liquid ratio of 1:5 and using 0.6 M ammonium chloride at room temperature for 1 hour, leaching rates of 54.39% for Zn and 86.23% for Cu were achieved.

Furthermore, the ammonia removal process proved to be highly effective in recovering Zn and Cu from the leachate, with impressive recovery rates of 95.99% for Zn and 98.90% for Cu under boiling and stirring condition at pH 9  $\pm$  0.1. The overall recovery rates of Zn and Cu from fly ash using the ammonium leaching and ammonia removal process reached 52.21% and 85.28%, respectively. The precipitate obtained from the recovery process exhibited significant metal concentrations, with 33.62% Zn and 14.19% Cu, making it an excellent candidate for further use as a raw material in metal smelting.

Moreover, the ammonium leaching process demonstrated exceptional reduction and dechlorination effects on fly ash. The mass of the treated fly ash was significantly reduced to only 30.63% of the original. Moreover, the chlorine content was lowered from 26.23% to a mere 0.84%. These results indicate that processed fly ash is more suitable for utilization in construction materials and as a raw material in cement production.

Overall, the findings highlight the potential of the ammonium-leaching processes for both effective metal recovery and a significant reduction in fly ash mass and chlorine content. These advancements contribute to the sustainable utilization of fly ash, positioning it as a valuable resource for various industrial applications.

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# STARTUP OF A CONTINUOUS FLOW GRANULAR SLUDGE-BASED ONE-STAGE PARTIAL NITRITATION/ANAMMOX PROCESS

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## INTRODUCTION

Characterized with significant reductions in oxygen consumption, organic carbon demand, and sludge production compared to traditional nitrification and denitrification technology, anammox process has proven to be a promising technology over the past three decades<sup>1,2,3</sup>. Anammox process often need to be combined with partial nitritation (PN) process, also known as the PNA process, because ammonium is the main type of nitrogenous contaminants in wastewater. This process provides the necessary electron acceptors for the subsequent anammox stage by converting part of the ammonium to nitrite, which is available for the subsequent anammox process<sup>4</sup>. As two different biological reactions are involved, PNA can be divided into two-stage and one-stage types in practical applications<sup>5</sup>. More than 80% of the world's full-scale PNA facilities are currently one-stage type<sup>1</sup>. In this study, a continuous flow granular sludge-based one-stage PNA reactor was operated, and the aim was to achieve a stable and efficient nitrogen removal performance in this reactor by regulating the aeration and closely monitoring the effluent nitrogen forms during the start-up phase of the reactor.

# MATERIALS AND METHODS

# **Reactor configuration and experimental conditions**

The reactor configuration used for the experiments was a continuous flow air-lifting reactor (ALR), comprised of a reaction zone with a volume of 5 L and a settling zone with a volume of 0.5 L. As shown in Fig. 1, The feed of the reactor is precisely controlled by a peristaltic pump. An air pump is used to deliver air into the reactor to provide oxygen for the reactor and realize the stirring function, and the air flow rate (AFR) is precisely regulated by a flow meter. The reactor temperature of approximately 25°C is regulated by a heating rods and a circulating chiller. The entire startup period was divided into five stages based on hydraulic retention time (HRT) as well as nitrogen loading. The operating conditions of the start-up experiments are shown in Table 1.

# Synthetic wastewater and inoculum sludge

Synthetic wastewater was used throughout the whole experiment. Ammonium chloride and sodium bicarbonate were added to provide NH<sub>4</sub><sup>+</sup>-N and HCO<sub>3</sub><sup>-</sup> respectively. The other ingredients were referenced to

previous studies<sup>6</sup>. The seed sludge was derived from reactor subjected to simultaneous nitrogen and phosphorus removal through the combination of a one-stage PNA and electrolysis with iron electrodes.



Fig. 1 The reactor configuration

# **Analysis Items**

Water samples were analyzed after filtration treatment in a 0.45  $\mu$ m filter head. Ammonium, nitrite, nitrate, were measured according to standard methods. Throughout the study, pH, DO, temperature, and oxidation-reduction potential (ORP) were measured using portable instruments. The collected sludge samples were properly stored at -20 °C for subsequent in-depth analysis of microbial community using 16S rRNA sequencing analysis.

| Table 1 The experimental conditions. |       |       |       |       |       |  |
|--------------------------------------|-------|-------|-------|-------|-------|--|
| phase                                | Ι     | II    | III   | IV    | V     |  |
| Time (d)                             | 1 16  | 17.24 | 25-   | 119-  | 161-  |  |
| Time (d)                             | 1-10  | 1/-24 | 118   | 160   | 173   |  |
| NH <sub>4</sub> +-N                  | 150.0 | 250.0 | 250.0 | 375.0 | 500.0 |  |
| HRT (h)                              | 18    | 18    | 12    | 12    | 12    |  |
| Temp (℃)                             | 25    | 25    | 25    | 25    | 25    |  |
| NLR                                  | 0.20  | 0.22  | 0.5   | 0.75  | 1     |  |
| (kg/m <sup>3</sup> d)                | 0.20  | 0.55  | 0.5   | 0.75  | 1     |  |

# **RESULT AND DISCUSSION** <u>Performance of the reactor</u>

The operating parameters are shown in Fig. 2, and the results of the experiments are shown in Fig. 3, where the

average effluent nitrogen species, NRE and NRR for each phase are shown in Fig. 4.

In phase I (1–16 d), the influent ammonium was kept at 150 mg/L, and the DO was kept at a low level by fine tuning of the AFR to promote the propagation and enrichment of AOB and AnAOB. During the pre-startup period of the reactor, its showed instability and lack of regularity in the values of nitrogen. Overall, the NRE remained at a high level.

In phase II (17-24 d), the influent ammonium was increased to 250 mg/L with the stable HRT. However, the effluent  $NH_4^+$ -N increased significantly during this phase, and its average concentration reached 80.79 mg/L with the accumulation of  $NO_2^-$ -N, resulting in a decrease in NRE to 26%, while NRR remained almost unchanged. It was hypothesized that the reason was the insufficient activity of AnAOB and AOB to effectively convert more  $NH_4^+$ -N and  $NO_2^-$ -N.

In phase III (25-118 d), the NLR raised to 0.5 kg/m<sup>3</sup>d by shortening the HRT. The increase of effluent  $NH_4^+$ -N appeared. On the 39th day, the effluent  $NH_4^+$ -N increased further due to an electrical outage (trip) in the laboratory. Immediately afterward, on the 40th day, the internal mixing system of the reactor became clogged, resulting in a continuous increase of effluent  $NH_4^+$ -N. After adjustment, although the effluent  $NH_4^+$ -N decreased, it was high. Meanwhile, the effluent  $NO_3^-$ -N gradually increased and exceeds the theoretical  $NO_3^-$ -N calculated based on the stoichiometric formula, and has been maintained at a high level since then. The increase of effluent  $NO_3^-$ -N was accompanied by the decrease of effluent  $NO_2^-$ -N at less than Img/L. it was inferred that

one of the reasons for the persistent non-decrease of NH<sub>4</sub><sup>+</sup>-N concentration in the effluent is the insufficient source of inorganic carbon required by the microorganisms ( $HCO_3^{-}/NH_4^{+}-N=1((molar ratio))$ ). Therefore, during the 67th day, the influent NaHCO3 was increased and a decrease in the effluent NH<sub>4</sub><sup>+</sup>-N was observed. However, subsequent inspection also revealed that the chemical determination failure. After these problems resolved, the effluent  $NH_4^+-N$ was significantly reduced. At the 97th day, a small aperture aeration head was introduced for aeration to avoid large disturbances and achieve higher oxygenation<sup>7</sup>. The effluent NH<sub>4</sub><sup>+</sup>-N decreased significantly (from 118.77 mg/L to 20.42 mg/L) and the NRE was elevated, with an average NRE of 39.46%.

After the NRE reached 60%, the NLR was increased to 0.75 kg/m<sup>3</sup>d and 1.0 kg/m<sup>3</sup>d by keeping the HRT unchanged while elevating the influent ammonium concentration, and the startup period entered the phase IV (119-160 d) and final V (161-173 d) phases, respectively. At the beginning of these two phases, the effluent  $NH_4^+$ -N increased sharply, which was due to the sudden increase of influent ammonium, and the

microorganisms had not yet adapted to this high environment. After the reactor was operated for 10 d and 5 d in the fourth and final phases, respectively, the effluent  $NH_4^+$ -N decreased rapidly, and the maximum decrease could be from 150 mg/L to 1.93 mg/L. At the same time, the average NRE was significantly increased from 39±11% in the phase III to 64±11% and 77±8%, respectively, and the maximum NRE even reached 86% in phase V.



Fig. 2 The operating parameters during the whole start-up experiment.



Fig. 3 Variation of nitrogen compounds concentrations and evolution of NRR, NRE, NLR.



Fig. 4 The average value of various nitrogen and NRR, NRE for each phase.

For eliminating effluent nitrate in phase III, which was mainly speculated attributed to the growth and propagation of NOB inside the reactor, the influent NH<sub>4</sub><sup>+</sup>-N increased in the fourth stage, aiming to inhibit the activity of NOB by increasing the free ammonia (FA) concentration. However, the experimental results did not show a decrease in effluent nitrate. Seed sludge was previously used to simultaneous nitrogen and phosphorus removal experiments by electrolysis of iron in a one-stage PNA with iron electrodes. Based on this, it was hypothesized that the sludge may contain high levels of iron, which in turn promotes the growth and proliferation of microorganisms associated with iron metabolism. Thus, the microbial community analysis was conduced.

# Microbial community

Sludge samples before the lifting of the inorganic carbon source (labeled S1) and after the lifting for a period of time (labeled S2) was collected and analyzed by 16S rRNA sequencing. In Fig. 5, based on the results of genus-level analyses, it was found that the abundance of main functional genus, Nitrosomonas, Candidatus Kuenenia, and Candidatus Brocadia, increased after the increase of inorganic carbon sources. This finding supports previous speculations that the microbial inorganic carbon source requirements were not being adequately met by microbial inorganic carbon sources before phase IV. Meanwhile, the sequencing results also confirmed that Nitrospira, associated with nitrite oxidation was present in reactor system with abundance of 0.14%. In view of this, further experimental verification is needed regarding whether the nitrite oxidation process actually occurs in the reactor. At the same time, a high abundance of Ferruginibacter was detected, which is an iron-reducing bacterium (FRB), closely associated with iron metabolism processes and plays a key role in the Feammox process<sup>8, 9</sup>. A high abundance of this bacterium was detected in the reactor (5.89% abundance before the inorganic carbon source was raised and 7.50% abundance after the inorganic carbon source was raised). If the Feammox does exist in the reactor, this would provide a plausible explanation for the abnormally high nitrate in the effluent: Ferruginibacter competes with the AnAOB for ammonium, converting it to nitrate. As a result, less ammonium is available to AnAOB, which instead reacts with the converted nitrite and the remaining ammonium, resulting in a lower accumulation of nitrate in the effluent. In addition, Denitratisoma<sup>10</sup> and Thermomonas<sup>8</sup>, which are associated with nitrate-dependent ferrous oxidation (NDFO), were also detected in the reactor, and their abundances after the elevated inorganic carbon source were 2.42% and 0.24%, respectively. This result suggests that the NDFO process may be occurred simultaneously inside the reactor, facilitating the cycling between Fe(II) and Fe(III). Of course, the above is only based on speculation based on the operation of the reactor and the results of the microbial community analysis. In order to verify whether these reactions are actually occurring, we need to carry out further activity experiments and test the iron content in the incoming and outgoing water and sludge to obtain more direct and conclusive evidence.



Fig. 5 The microbial community: genus level.

#### CONCLUSION

The one-stage PNA reactor was operated for five phases and ultimately exhibited up to 86% NRE. However, the average effluent nitrate exceeded the expected value. Based on the the microbial community analysis, the presence of Ferruginibacter was detected, which was closely associated with the Feanmox that affected the concentration of nitrate in the effluent. The future study should verify the complex reaction mechanisms within the reactor and delve into effective strategies to reduce high effluent nitrate.

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# RESEARCH ON PRETREATMENT AND ENZYMATIC PROCESS OF LIGNOCELLULOSIC BIOMASS CORN COB

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# INTRODUCTION

Corn cobs are one of the main wastes from corn production, with an average of 1 kg of corn cobs for every 3 kg of corn. Corn cobs are rich in cellulose, hemicellulose and lignin, which are typical lignocellulosic biomass and can be used in microbial fermentation to produce biomass energy or chemicals. Lignocellulosic biomass is the most abundant renewable energy bioresource available today<sup>1</sup>. Due to its cellulose, hemicellulose and lignin are tightly interwoven to form a structure that is difficult to decompose, lignocellulosic biomass directly undergoes enzymatic digestion with low efficiency, and needs to be pre-treated prior to enzymatic digestion in order to improve the enzymatic efficiency and to release more fermentable sugars. The purpose of pretreatment is to dissolve hemicellulose and lignin, thereby changing the structure of the matrix and exposing the cellulose, thus significantly enhancing the accessibility of cellulose to the enzyme and improving the efficiency of the subsequent enzymatic reaction<sup>2</sup>. The composition of the different components of lignocellulose and the variations in their proportions depend on the biomass, the part of the plant material, and the stage of growth, etc., so that different biomasses cannot simply be treated with a uniform pretreatment technique. The appropriate pretreatment technology should not only maximize the hydrolysis yield of the raw material, but also minimize the formation of fermentation inhibitors during pretreatment and the impact on subsequent processes.

This paper focuses on the investigation of suitable pretreatment processes for corn kernels to ensure the efficiency of cellulosic hemicellulose saccharification while avoiding the production of fermentation inhibitors. Meanwhile, the parameters of the selected pretreatment process were optimized to obtain the best pretreatment process conditions, which resulted in the highest yield of fermentable sugars in corn cobs.

### MATERIALS AND METHODS

(1) Pretreatment of corn cobs

Lower temperature hydrothermal pretreatment (LTHP): dry corn cobs were wet ground and put

into an autoclave at 120 °C for 60 min. Acid pretreatment:  $H_2SO_4$  was added at 1% (v/v), and the rest was the same as LTHP. Alkali pretreatment: 1% (w/v) NaOH was added, and the rest was the same as LTHP. High temperature hydrothermal pretreatment (HTHP): dry corn cobs were wet ground and put into a highpressure reactor at 160 °C for 30 min. After pretreatment, remove the reaction material, cool to room temperature, centrifugal separation, the supernatant is the pretreatment solution, the solid part of the water washing to neutral and drying to record the mass for the calculation of solid recovery rate.

(2) Enzymatic saccharification

The untreated corn kernel material was used as the control group, and the pH of the solution was adjusted to 4.8 with 3 mol/L  $H_2SO_4$  or NaOH, cellulase was added according to 20 FPU/g of corn kernel, and the supernatant was taken at the end of the enzymatic digestion to determine the concentration of fermentable sugars in the enzymatic solution.

(3) Methods of analysis

The content of cellulose, hemicellulose and lignin in the corn kernels before and after pretreatment was determined according to the standard method of the National Renewable Energy Laboratory (NREL). Concentrations of fermentable sugars and inhibitors (formic acid, acetic acid, 5hydroxymethylfurfural, and furfural) in the corn kernel pretreatments and enzyme digests were determined by high performance liquid chromatography (HPLC).

#### **RESULT AND DISCUSSION**

#### (1) Determination of pretreatment

Under the same enzyme digestion conditions, the total sugar yield of corn kernel after pretreatment was as follows: acid pretreatment (67.3 g) >HTHP (65.6 g) > alkali pretreatment (56.4 g) > LTHP (39.8 g), and the total sugar yields of the acid pretreatment and HTHP were 85.9% and 84% respectively (F1). Although the former enzyme digestion and saccharification were slightly better than the latter, but the acid pretreatment was more corrosive to the equipment and the material after pretreatment needed a lot of water washing to

meet the required pH value of the enzymatic digestion. Although the enzymatic saccharification effect of the former was slightly better than that of the latter, the acid pretreatment had a stronger corrosive effect on the equipment and the pretreated material needed a lot of water washing to meet the pH value required for enzymatic digestion. In addition. the concentration of inhibitors produced by acid and alkali pretreatment is higher than that of hydrothermal pretreatment, so hydrothermal pretreatment is greener and more efficient in comparison. Considering the treatment effect and economic and environmental benefits, HTHP was determined to be the most suitable pretreatment method for corn cobs.





(2) Optimization of pretreatment process conditions

The optimal conditions for the high-temperature hydrothermal pretreatment of corn cobs were: solid-liquid ratio of 1:9, temperature of 160°C, pretreatment time of 40 min (F2, F3, F4). Under which the pretreatment corn cobs were enzymatically digested with a fermentable sugar yield of 82.9 g and a total sugar yield of 95.5%.



Fig.2 Effect of pretreatment temperature on the effect of enzymatic saccharification



Fig.3 Effect of pretreatment time on the effect of enzymatic saccharification



Fig.4 Effect of different solid-liquid ratios on enzymatic hydrolysis effect

# CONCLUSION

High temperature hydrothermal pretreatment was selected among the four pretreatment methods. At the same time, the parameters of the selected pretreatment process were optimized, and the best pretreatment process conditions were obtained. Finally,82.9 g of fermentable sugar was obtained from 100 g of pretreated corn kernels after enzymatic digestion, and the total sugar yield was 95.5%.

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# Research progress of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> based photocatalytic treatment of

# landfill leachate

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**Abstract:** Landfill leachate is a complex high-concentration organic wastewater with the characteristics of a large number of pollutants, high ammonia nitrogen concentration, and a variety of heavy metal ion types and high content. Due to the poor operation effect of the conventional treatment process for landfill leachate in China, it is difficult to meet the standard requirements for water quality indicators. In order to solve these problems as much as possible and combine the current commonly used treatment process in China, the photo catalytic technology in physical-chemical treatment can effectively degrade the difficult-to-degrade pollutants in wastewater, so synthesizing cheap and efficient catalysts suitable for treating landfill leachate has become a research hotspot for landfill leachate. The photo catalytic agent is the core of photo catalytic technology, and Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>-based photo catalytic materials have shown good catalytic ability. However, the photo catalytic performance of pure Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> needs to be improved. Currently, the regulation of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> mainly includes improving the morphological structure, constructing oxygen vacancies, doping or metal loading.

Keywords: photocatalytic technology, landfill leachate, Bi2O2CO3

# INTRODUCTION

With the rapid development of China's economy and the improvement of residents' living quality, the amount of urban waste generated, transported, and treated has increased year by year. Currently, the national waste treatment pattern is mainly incineration with landfill as a supplement. According to the China Statistical Yearbook, the amount of safe disposal of urban waste in China in 2021 was 248,393,000 tons, of which 52,085,000 tons were disposed of by landfill, accounting for 20.97%, and 180,197,000 tons were incinerated, accounting for 72.46% of the safe disposal [1]. It is reported that 0.05~0.2 t of waste leachate is generated in the life cycle process of urban waste transportation and treatment, such as landfill and incineration [2]. Waste leachate has complex components and high pollutant content, containing toxic or biologically non-degradable compounds such as ammonia, heavy metals, organic halogen compounds, humic acids, and fulvic acids [3]. At present, the treatment of waste leachate from landfills in China is mainly based on conventional biological treatment. This method has good treatment effects on the biodegradable organic matter in the leachate, and the process and operating costs are low. However, the single biological method is not completely effective in the biological treatment of waste leachate, and it cannot make the leachate meet the discharge standard. Based on this, this study conducts in-depth treatment of the biological effluent of waste leachate to achieve its discharge standard.

1.The dilemma of treating the

# difficult-to-degrade organic matter in landfill leachate effluent

The pollutant and difficult-to-treat nature of landfill leachate mainly stems from the complexity and variability of its components. The vague understanding of the properties of the research object, landfill leachate, has led to a certain degree of blindness in the treatment process. In order to explore suitable advanced treatment processes and solve the problem of difficult-to-treat landfill leachate effluent, many scholars have conducted studies on the composition and properties of landfill leachate.

Some studies have shown that the water-soluble organic matter in landfill leachate tailwater mainly consists of hydrophobic humic substances and non-humic substances (quasi-hydrophilic substances). The hydrophobic humic substance, humic acid (HA), has a high aromaticity, while fulvic acid (FA) has a high content of carboxylic acids. HA and FA have benzene ring structures and may contain alcohol hydroxyl or phenolic hydroxyl groups and carboxylic acid functional groups. The quasi-hydrophilic substances have more oxygen functional groups, which may be carboxylic acid functional groups, and they may also have some hydroxyl functional groups and fatty chain structures, with less nitrogen content and the possibility of containing triple bonds and double bonds [5,6]. Yang Zhi [7] used GC-MS to study the trace organic matter in landfill leachate before and after biological treatment, and the results showed that after biological treatment, 55 kinds of organic matter were detected in the leachate effluent, mainly composed of alkenes, alkanes, alcohols, and esters, with a decrease in acidic substances and toxic organic matter. Alkenes and cycloalkanes may be produced by the oxidation of straight-chain long alkanes in the influent, and alcohols and esters are also oxidation intermediates of hydrocarbons. These substances constitute the difficult-to-degrade organic matter in landfill leachate, which has become a bottleneck.

The research group used GC-MS to analyze the material composition of leachate tail water (landfill leachate effluent at the later stage of bioreactor operation), and searched it through the NIST database, and the organic compounds present in it include alkanes containing groups (from methane to octadecane), esters, biphenyls, phenols, oxalic acid, ketones, ethers, aldehydes, alcohols, etc., and more than 100 kinds of organic compounds, among which alkane organic compounds are the main ones. The search for 16 organic compounds with high content in the total ion current map showed that the organic pollutants included in the leachate tail water were alkanes, phenols and esters. Among them, there were 12 alkane compounds, 3 phenol compounds and 1 ester compound, of which the highest organic matter was biphenyl, accounting for 12.77%. The organic matter of alkanes and aromatic hydrocarbons contained in it is similar to that of previous studies on the composition of leachate [10], and the characteristics of alkanes aromatic and hydrocarbons that are difficult to degrade also correspond to the characteristics of leachate that are difficult to treat.

2.Refractory organic pollutants in leachate tail water are the main bottleneck of effective leachate treatment, and photocatalytic oxidation technology, as a new advanced oxidation technology, has certain advantages in degrading leachate tail water.

There are a large number of refractory organic compounds in the biological effluent of landfill leachate, which is persistent in the water environment. The random discharge of these pollutants will have a negative impact on the surrounding aquatic ecological environment and increase the potential toxicity to aquatic organisms. Therefore, in the selection of landfill leachate treatment process, it is advisable to adopt a method that can preferentially remove such substances and combine it with biological treatment.

At present, the mainstream leachate treatment process is a combination of "pretreatment + biological treatment + advanced treatment". Among them, the pretreatment generally adopts physical and chemical treatment, including coagulation, blowing, precipitation, adsorption, etc., the main purpose of which is to reduce the concentration of SS and remove some heavy metal ions; The conventional processes of biological treatment include upflow anaerobic sludge bed (UASB), upflow sludge bed filter (UBF), membrane bioreactor (MBR), A<sub>2</sub>/O, A/O, etc., and the main task of biological treatment is denitrification and carbon removal. According to relevant literature, the advanced treatment methods of leachate commonly used in China are mainly physical and chemical methods. Techniques for the removal of refractory biodegradable organic matter from leachate under mild conditions include adsorption, membrane technology, flocculation and sedimentation, wet catalytic oxidation, supercritical oxidation, and electrochemical and ultrasonic [11,12]. Among them, the adsorption method [13], membrane treatment method [14], and flocculation precipitation method [15] are mainly used to concentrate or transfer pollutants, but do not realize the transformation or degradation of pollutants, and are easy to cause secondary pollution. Technologies that can transform or degrade refractory biodegradable organic matter in leachate, such as wet catalytic oxidation [16] and supercritical oxidation [17], are realized under extreme conditions such as high temperature and high pressure. Other methods, such as electrochemistry [18] and ultrasonic [19], are energy-intensive, making it difficult to achieve large-scale utilization.In contrast, photocatalytic oxidation, as a new advanced oxidation technology, is developed on the basis of photochemical oxidation, which has strong oxidation ability, no secondary pollution, can be

carried out at room temperature and pressure, and has the characteristics of environmental protection, energy saving and high efficiency, and has begun to receive attention in the field of leachate treatment. Photocatalysis, as an emerging solar energy utilization technology, is of great significance to help China achieve the "double carbon" goal.

Photocatalytic technology is a technology based on the special band structure of semiconductors, generally speaking, semiconductor photocatalysts have special discontinuous band structures, including valence band (VB) and conduction band (CB), and different semiconductor materials have different widths of bandgap between the valence band and the conduction band. The size of the band gap is expressed by the band gap width (Eg). The light absorption threshold  $\lambda g$  and bandgap Eg of semiconductor materials satisfy  $\lambda g=1240/Eg$ [20]. The reaction mechanism of photocatalytic degradation of organic matter is shown in Figure 1. (1) When the excitation light with energy greater than or equal to the Band Gap (Eg) of the semiconductor is irradiated the on semiconductor, the electrons on the Valence Band (VB) absorb the light energy and undergo an energy level transition to the Conduction Band (CB), thus forming an electron-hole pair (e--h+); (2) There are two reaction pathways for electron-hole pairs, the first is that electron-holes can recombine to rebalance their internals; The second is to overcome the electrostatic force under the influence of the built-in electric field to separate the two and migrate to different positions on the semiconductor surface. (3) Based on the unique strong redox properties of the two, the corresponding chemical reactions with organic and inorganic substances are carried out at the relatively stable active reaction sites on the semiconductor surface. h+ has strong oxidizing properties, which can directly oxidize the organic matter adsorbed on the surface of the catalyst, or react with H2O and OH- to form

hydroxyl radicals with strong oxidizing properties (· OH); e- can reduce dissolved oxygen to superoxide radicals with strong oxidizing properties ( $\cdot$  O<sub>2</sub>-),  $\cdot$  O<sub>2</sub>- can be directly involved in the degradation of organic matter, and can also be further reduced to  $\cdot$  OH  $\circ$  In the process of photocatalytic oxidative degradation,  $\cdot$  O<sub>2</sub>-, h+, and  $\cdot$  OH is the main active species that degrades pollutants, and these free radicals oxidize a variety of organic pollutants to harmless inorganic substances such as CO<sub>2</sub>, H<sub>2</sub>O, and other small molecules [21,22].



Fig.1 Diagram of the photocatalytic reaction mechanism

At present, some experts and scholars at home and abroad have introduced photocatalysis into the field of leachate treatment. Azadi et al. [23] compared the efficiency of N, P, and N-P TiO<sub>2</sub> in the treatment of leachate under visible light irradiation, and the results showed that the removal rates of Leachate with initial COD of 2050 mg/L for W-TiO<sub>2</sub> nanoparticles, C-TiO<sub>2</sub> nanoparticles, and W-C-TiO2 nanoparticles were 46%, 60%, and 64%, respectively, after 46 h of irradiation. Sama et al. [24] explored a W-C co-doped TiO<sub>2</sub> nanoparticle fixed photoreactor to overcome the limitations of mass transfer and aeration during immobilized photocatalysis, and found that the removal rate of COD reached 84% under the optimal conditions of initial COD value of 550 mg/L, light intensity of 40 W, coating density of 10.59 g·m-2 and leachate flow rate of 1 L·min-1. Chu et al. [25] prepared a novel visible light-driven photocatalyst (Bi<sub>2</sub>WO6/BiOI/g-C<sub>3</sub>N<sub>4</sub>) doping by

Bi<sub>2</sub>WO6/BiOI nanoparticles with graphite nitride carbon  $(g-C_3N_4),$ and cured Bi<sub>2</sub>WO6/BiOI/g-C<sub>3</sub>N<sub>4</sub> with polytetrafluoroethylene (PTFE) and boric acid (H3BO3), and photocatalytically degraded the leachate of municipal waste transfer station (MWTS) for 28 h, with a COD removal rate of 56.1%, the TOC removal rate was 50.4%. Jiang Baojun et al. [26] prepared TiO<sub>2</sub>-y-Al<sub>2</sub>O<sub>3</sub> composite catalysts by liquid-phase co-precipitation method, and found that when the molar ratio of Ti(SO4)<sub>2</sub> to Al<sub>2</sub>(SO4)3·18H<sub>2</sub>O was 1:2, the mass fraction of polyethylene glycol was 1.25%, the calcination temperature was 650°C, the mass ratio of TiO2-7-Al2O3 to the mass of landfill leachate was 1.75, the reaction time was 90 min, and the leachate pH was 3, the sunlight/the removal rates of COD and NH4+-N by TiO<sub>2</sub>-y-Al<sub>2</sub>O3 reached 81.97% and 54.95%, which were slightly higher than those of COD and NH4+-N under the optimal reaction conditions of UV/TiO<sub>2</sub>.

Meeroff et al. [27] photocatalytically degraded 130-330 mg/L of leachate by TiO2 and found that the COD removal rate could reach 70% after 4 h of treatment, and the BOD<sub>5</sub>/COD value increased from 0.09 to 0.14. Sung et al. [28] treated the landfill leachate after biological pretreatment with P<sub>2</sub>5 TiO<sub>2</sub> at pH 4, and after 10 h of photocatalysis, 56% of the COD could be removed. Jia et al. [29] used UV-TiO<sub>2</sub> photocatalytic oxidation of landfill leachate, and the removal rates of color, TOC and COD were as high as 97%, 72% and 60% when the treatment time was 60 h, indicating that the main chromatic substances humic acid and azo compounds in the landfill leachate were significantly photocatalytically degraded. The results of GC/MS analysis showed that the landfill leachate DOM contained as many as 72 kinds of organic pollutants, including more ketones, alcohols and carboxylic acids, while in the photocatalytic 72 h treatment solution, the number of organic compounds decreased to 44,

and there were more esters, alcohols and ketones, while the reduction of carboxylic acids was the most obvious, indicating that carboxylic acids were more susceptible to photocatalytic degradation.

# 3. Photocatalysts are the core of photocatalytic technology, and Bi<sub>2</sub>O<sub>2</sub>CO3-based photocatalytic materials show good catalytic ability.

At present, there are some disadvantages of inorganic semiconductor photocatalysis represented by TiO<sub>2</sub>, such as low quantum efficiency, low solar energy utilization rate (only absorbing less than 5% of ultraviolet light in sunlight), weak selectivity, and poor stability. The above problems are currently the focus of research in the field of photocatalysis, and further research on these issues is not only expected to achieve a great breakthrough in the basic theory of photocatalysis, but also conducive the wide application to of photocatalytic technology in the fields of energy development and environmental governance. In order to solve these problems, one of the core research directions is the development of new and efficient visible light-responsive inorganic semiconductor photocatalysts. In recent years, bismuth-based materials, such as BiVO<sub>4</sub> [30], Bi<sub>2</sub>WO<sub>6</sub> [31], Bi<sub>4</sub>O5Br<sub>2</sub> [32], and Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [33], have been favored by researchers due to their low cost, simple synthesis, and abundant resources.

Bismuth oxycarbonate (Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>) has been widely used in various fields as a low-cost and environmentally friendly bismuth material. Similar to other bismuth materials, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> has been shown to be a typical "sillén" phase and a member of the Aurivillius structural oxide family [33,34]. Depending on the synthesis method, the bandgap width of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> can be between 2.85~3.85 eV, the potential of CBM can be -0.49~0.2 eV, and the potential of VBM can be 2.87~3.58 eV, which has the ability to produce  $\cdot$ O<sub>2</sub>- and  $\cdot$ OH [35]. The CBM of  $Bi_2O_2CO3$  is mainly composed of Bi 6p orbitals, the VBM is mainly composed of  $O_2p$  orbitals, and the valence band corrected energy level position is contributed by carbon element.

Thus, the bandgap transition of electrons occurs mainly in the O<sub>2</sub>p and Bi6p orbitals. Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is composed of alternating bismuth oxygen layer ([Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup>) and carbonate layer  $[CO_3]^{2-}$  layers, the plane of the  $[CO_3]^{2-}$  layer is orthogonal to the plane of the  $[Bi_2O_2]^{2+}$  layer [36], and the charge distribution between the two layers is uneven, so that the static internal electric field is generated, which is conducive to the separation of photoexcited carriers. The interlayer distance between the adjacent two layers of [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> can reach 0.684 nm, which is wider than that of other semiconductor catalysts of the Aurivillius family, which will facilitate the diffusion and transfer of ROS and reactants, and the wider layer spacing will also make the strength of the static internal electric field stronger than that of other layered bismuth-based semiconductor materials, which is more conducive to the transport of light-excited carriers [37]. Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is an N-type indirect semiconductor with tunable bandgap with the possibility of visible light-driven reactions [38], and has a high oxygen atom density (62.5% of the overall structural oxygen atom percentage), which has significant benefits for the active sites of oxygen defects on the structural surface [39]. The presence of strong covalent bonds and van der Waals interactions between the atomic layers of Bi2O2CO3 allows it to maintain a stable chemical structure during photocatalytic reactions [40]. In addition, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> also has the characteristics of simple preparation process, wide range of sources, low cost, no secondary pollution, etc., which is an environmentally friendly material that can meet the needs of current green development. At present, the regulation of Bi2O2CO3 mainly includes the improvement of morphological structure, structural oxygen defects, doping, or metal

### loading [41].

# (1) Morphology control

The one-dimensional (1-dimensional) nanowires, nanotubes, and nanoparticle structures, two-dimensional (2-dimensional) nanosheet structures, and three-dimensional (3-dimensional) microsphere structures of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> compounds have been successfully prepared and applied to photocatalytic reactions [42–47]. Usually, the template method is used to obtain some special topography structures. For example, ultrathin nanosheets with higher photocatalytic activity can be synthesized with the assistance of templates such as Cetyl Trimethyl Ammonium Bromide (CTAB) and Sodium Dodecyl Sulfonate (SDS) [48]. However, the large-scale application of template synthesis will be limited by cumbersome steps such as template modification, precursor attachment, and template removal, and unnecessary impurities may appear in the process of template removal. According to the special layered structure of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, the growth rate along one axis is lower than that of other axes, and the 3D morphology of sheets or nanosheets can be formed. Therefore, in order to avoid the shortcomings of the template method, a more convenient and efficient template-free method can be used to regulate the morphology and structure of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.

# (2) Metal loading

Several of metal/Bi2O2CO3 types nanocomposites have been reported, including Ag/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, Pt/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, and Bi/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [49-51]. Compared with pure Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> microspheres, the light absorption and nitrogen dioxide removal rates of the prepared Ag nanocrystallized Bi2O2CO3 layered microspheres were significantly enhanced due to the surface plasma resonance (SPR) effect of silver (Ag) [52]. Other precious metal particles loaded on the surface of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> also exhibit a similar phenomenon. Notably, the researchers found that the inexpensive semi-metallic bismuth (Bi) also has an SPR effect, which can replace precious metals to enhance photocatalytic activity and photochemical stability. The use of thiourea as a reducing agent can reduce  $Bi^{3+}$  to metal Bi on  $Bi_2O_2CO_3$  microspheres, and ethylene glycol as a reducing agent can also achieve one-step control of the synthesis of metal-supported photocatalysts [53]. In general, metal/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanocomposites all have similar photocatalytic mechanisms, and the enhanced photocatalytic activity is mainly due to the fact that the metal nanoparticles supported on the surface of the photocatalyst induce the SPR effect, improve the light absorption efficiency, and promote the separation of photogenerated electron-hole pairs.

(3) Construct oxygen vacancies

In recent years, the introduction of oxygen vacancies (OVs) into metal-oxide semiconductors has been a simple and effective method to improve photocatalytic performance by enhancing sunlight utilization and promoting surface ROS generation [54]. OVs can not only reduce the transfer resistance of photogenerated carriers, but also effectively delay their recombination. So far, the methods of introducing OVs include heat treatment, solvothermal and reduction. For example, Dong et al. [55] vacuum heat treatment of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> at 250°C, 275°C, and 300°C respectively could obtain black microspheres with defects, and the photocatalytic nitrogen oxide removal rate could be increased by 2.6 times, 3.14 times, and 2.82 times, respectively. The solvothermal method uses glyoxal as the reducing agent, and the concentration of OVs in Bi2O2CO3 can be adjusted by continuously changing the concentration of glyoxal, so as to achieve an adjustable light absorption range and band structure. Related studies have shown [56] that the emergence of OVs not only makes Bi2O2CO3 present an intermediate energy level between the valence band and conduction band, greatly expanding the light absorption from 360 nm to 520 nm, but also greatly promotes the generation

and separation of photogenerated electrons and exhibiting holes. thus highly promoted photocatalytic performance. However, while OVs improve their photocatalytic performance, their stability during the reaction will also become another key factor affecting the photocatalytic degradation efficiency. It has been reported that OVs may be filled with reactant molecules and inactivated as the reaction progresses [57]. For example, the photocatalyst formed by the introduction of OVs into the surface of Bi2O2CO3 by sodium borohydride (NaBH4) reduces the photocatalytic activity due to the partial loss of OVs on the surface during the continuous reaction [58]. Fortunately, researchers have found some effective measures to improve the stability of OVs. For example, Bi nanoparticle-modified oxygen-vacant metal Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanosheets were prepared [59]. Bi metal nanoparticles can act as active sites to activate oxygen and water molecules so that they do not fill into OVs, preventing OVs from being inactivated, thus maintaining stable photocatalytic activity. In addition, taking advantage of the synergistic effect of OVs and element doping, the photocatalyst can also exhibit excellent photocatalytic stability and maintain good performance after multiple cycles of photocatalytic reactions [60].

(4) Construction of heterojunctions

The construction of heterojunction can significantly improve the separation efficiency of photogenerated carriers and promote the absorption of light by the catalyst. Therefore, the photocatalytic performance of the catalyst is significantly improved. Majhi et al. [61] synthesized CdS/BiOBr/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (CDS) by a one-step hydrothermal method, and the absorption edge of the ternary heterojunction was significantly redshifted, and the absorption of visible light was also significantly increased. The degradation rate of atrazine was as high as 95% after 30 minutes of visible light. The electron transfer of double-Z heterojunction promoted the redox reaction of active species, so the photocatalytic performance of ternary heterojunction was significantly improved. Li et al. [38] synthesized the heterojunction of Bi<sub>2</sub>O<sub>4</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and synthesized Bi<sub>2</sub>O<sub>4</sub> hydrothermally. Then, Bi2O4 was added to rhodamine B for several hours to prepare Bi<sub>2</sub>O<sub>4</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> binary heterojunction, and the absorption edge was blue-shifted, because the conduction band position of Bi2O4 was more negative than that of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, the electrons were excited and transferred to Bi2O2CO3 and then formed superoxide radical•O2- through chemical reaction, which improved the separation efficiency of photogenerated electrons and holes, so the performance of degrading phenol and ciprofloxacin was significantly improved. Zhao et al. [62] calcined melamine to prepare g-C<sub>3</sub>N<sub>4</sub>, and then added g-C<sub>3</sub>N<sub>4</sub> to bismuth nitrate and urea systems to hydrothermally prepare g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. The photogenerated electron and hole recombination efficiency of heterojunction is significantly reduced, and the efficiency of charge transfer and separation is improved. The degradation performance of g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was 11.6 times higher than that of bismuth oxycarbonate under full-spectrum irradiation. Therefore, the construction of heterojunctions can significantly improve the photocatalytic performance of materials.

# CONCLUSION

The  $Bi_2O_2CO_3$  based photocatalytic material exhibits good catalytic ability, but the photocatalytic performance of pure  $Bi_2O_2CO_3$ needs to be improved. In future research, there are several directions for  $Bi_2O_2CO_3$  based photocatalytic treatment of leachate effluent from garbage. Regulation of  $Bi_2O_2CO_3$ , improvement of morphology and structure, construction of oxygen defects, doping or metal loading, and other methods.

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## STUDY ON OPTIMIZATION THE DOSAGE OF LOW COD CONTENT HEAVY METAL IMMOBILIZATION AGENT

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#### **1.INTRODUCTION**

In Japan, organic chelate-based heavy metal immobilization agents have been seen as problem because they increase the COD load at landfill sites, making water treatment more difficult and lengthening the time from closure to decommissioning.

Meanwhile, inorganic phosphate-based heavy metal immobilization agents are expected to help solve this problem because they have a low COD content.

However, if there is a large amount of unreacted slaked lime in the incineration fly ash, additional equipment for neutralizing agent to adjust the alkalinity is required, and there are problems such as an increased burden on on-site staff for inventory management.

To cope with these issues, we applied slaked lime mixed with amorphous aluminum hydroxide, which has the effect of reducing the alkalinity of fly ash.

Furthermore, by controlling the chemical injection so that the amount of inorganic phosphate-based heavy metal immobilization agent dosage was optimized.

This article describes the results of field test.

#### 2.MATERIALS AND METHOD

#### 2.1 Study site

Evaluation tests were conducted at incineration facility A shown in Table 1.

| <b>T</b> 11 | 4 | T 111    |   |          |
|-------------|---|----------|---|----------|
| Laple       | н | Facility | A | overview |

| Index                 | Specifications              |
|-----------------------|-----------------------------|
| waste type            | municipal solid waste       |
| Incinerator model     | gasification melting furace |
| Incineration capacity | 150 tons/day/furnace        |

#### 2.2 Chemicals

The chemicals used in this evaluation test are shown in Table 2.

| Table 2 Overview of chemical agent                  |                       |                               |  |
|---|-----------------------|-------------------------------|--|
| Index   | convential chemical   | examined chemical             |  |
| acidic gas  | cloked lime           | slaked lime with              |  |
| neutralization agent                                | slakeu lillie         | amorphous aluminum hydroxide* |  |
| hoory motol   | aluminum sulfate      |                               |  |
| immobilization agent                                | and                   | phosphate-based agent         |  |
| minoonizaton agent                                  | phosphate-based agent |                               |  |
| *amorphous aluminum hydroxide blending ratio : 15 % |                       |                               |  |

#### 2.2.1 Conventional chemical

Slaked lime was used to treat acid gas, and an inorganic phosphate-based heavy metal immobilization agent was used to treat fly ash. Aluminum sulfate was also used to neutralize the excess alkaline content of fly ash because phosphate-based heavy metal immobilization agent was consumed by the alkaline content.

#### 2.2.2 Examined chemical

Slaked lime mixed with amorphous aluminum hydroxide was used for examination. The blending ratio of amorphous aluminum hydroxide was determined to 15% based on its ability to reduce the alkalinity of fly ash and pre-evaluation test.

## 2.2.3 COD leaching potential of heavy metal immobilization agent

Table 3 shows the comparison of the COD load of the phosphate-based agent used in this study with a chelate agent. It was confirmed the COD load of the phosphate-based agent is lower than that of a chelate agent.

| Tuble b companion of COD Milliouening concentration |                         |  |  |
|---|-------------------------|--|--|
| type of heavy metal                                 | leaching concentration* |  |  |
| immobilizaiton agent                                | mg/l                    |  |  |
| phosphate-based agent                               | 2,160                   |  |  |
| chelate agent                                       | 13,000                  |  |  |

Table 3 Comparison of  $\text{COD}_{Mn}$  leaching concentration

X Japan Leaching Test 13th method (JLT 13)

#### 2.3 Chemical dosage control

Table 4 shows the chemical dosage control method for the acid gas treatment agent and aluminum sulfate.

| Table 4                      | Table 4 method of chemical dosage control    |  |  |  |
|------------------------------|--|--|--|--|
| Index convential way         |  | examined way                                 |  |  |
| acidic gas<br>neutralization | PID control                                  | Our proprietary control device $^{*1}$       |  |  |
| heavy metal neutralization   | Our proprietary control device <sup>*2</sup> | Our proprietary control device <sup>*2</sup> |  |  |

\*1: for slaked lime(Figure 1-1)

\*2: for aluminum sulfate(Figure 1-2)

#### 2.3.1 acidic gas neutralization agent dosage control

Our proprietary chemical injection control device shown in Figure 1-1 was used in the evaluation test to control the dosage amount of acidic gas treatment agent so that there is no excess or deficiency, and to reduce the alkalinity derived from unreacted slaked lime in the fly ash. This control device has multiple functions and can be easily optimize the facility's exhaust gas conditions.

#### 2.3.2 fly ash neutralization agent dosage control

To control the dosage rate of aluminum sulfate, a proprietary dosing control device that can measure the alkalinity(\*) of fly ash on-site was used (Figure 1-2). The fly ash alkalinity at which aluminum sulfate was no longer necessary was confirmed in a preliminary evaluation to be 100 mg-CaCO<sub>3</sub>/g-ash. Therefore, in subsequent evaluations, the target was to keep the alkalinity in the fly ash below 100 mg-CaCO<sub>3</sub>/g-ash. And the dosage rate of phosphate-based heavy metal immobilization agent was also fixed at 5.5% per ash.

%Fly ash alkalinity was measured by dissolving the ash in a specified amount of pure water, then titrating it with acid, and the amount titrated to reach a pH of 8.3 was expressed in terms of calcium carbonate.



Figure 1-1 slaked lime dosage controller Figure 1-2 aluminum sulfate dosage controller



Figure 2 relationship between fly ash alkalinity and dosage rate of heavy metal immobilization agent

#### 2.4 Evaluation method

The evaluation test conditions are shown in Table 5. A comparison was made between the conventional condition of a combination of slaked lime and PID control (CASE 1), CASE 2 in which the control method for the acid gas treatment agent was changed to our proprietary device, and CASE 3 in which two conditions, the acid gas treatment agent, and the control method, were changed. The evaluation items were the fly ash alkalinity under each condition. Table 5 evaluation test condition

| CASE | acidic gas neutralization agent                  | dosage control method  |  |  |
|------|--|------------------------|--|--|
| 1    | slaked lime                                      | PID control            |  |  |
| 2    | slaked lime                                      | slaked lime controller |  |  |
| 3    | slaked lime with<br>amorphous aluminum hydroxide | slaked lime controller |  |  |

#### **3.RESULTS AND DISCUSSION**

#### 3.1 Flue gas trends

Figure 3-1 shows the trend of acid gas treatment under PID control, and Figure 3-2 shows the trend of acid gas treatment under our proprietary control. Compared to PID control, these results confirmed that the fluctuation in HCl concentration was reduced with using our slake lime dosage control device. And the dosage amount of slaked lime was reduced by approximately 8 % compared to conventional PID control.



#### 3.2 Fly ash alkalinity trends

Figure 4 shows the measurement results of fly ash alkalinity under each condition. Under conventional conditions (CASE 1), the average fly ash alkalinity was 132 mg-CaCO<sub>3</sub>/g-ash, and by changing the chemical injection control conditions, it reached 107 mg-CaCO<sub>3</sub>/g-ash (CASE 2). Under the conditions of CASE 3, in which the acid gas treatment agent was changed to amorphous Aluminum hydroxide mixed and our chemical injection control device was also used, the fly ash alkalinity reached a value close to 100 mg-CaCO<sub>3</sub>/g-ash. As a result, it is expected that heavy metals can be treated without fly ash neutralization agent.





As a result of this study, it was confirmed that the alkalinity derived from unreacted slaked lime in fly ash can be reduced and the applicability of low COD content phosphate-based heavy metal immobilization agent can be expanded.

In the future, we would like to apply this technology to other facilities as well, contributing to reducing COD and alkaline loads at landfill sites.

# CONSTRUCTION AND EVALUATION OF A USED PAPER SEPARATING SUPPORT SYSTEM USING DEEP LEARNING

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#### Abstract

Separation of used paper is an important issue to increase recovered paper and reduce waste. One solution to this issue is to use tools that make it easier to separate various recyclable and non-recyclable paper types. One such tool is the used paper separation support system, which utilizes image recognition AI. Purpose of this study is to build the used paper separation support system and to evaluate its accuracy. In this study, an AI technology called YOLO used as object detection method. As a result, this system achieved a mean Average Precision (mAP) score of 0.714, indicating that this image recognition-based system detects and identify 12 used paper categories with an accuracy rate of over 70%. We conclude with possibility of this system for separation of used paper.

#### Introduction

In Japan, recovered paper collection rate has reached about 80% and recovered paper utilization rate is 66% In recent years [1]. This rate is one of the highest in the world.

One of issues to increase the collection and utilization rate of recovered paper further in the future is to correctly separate used paper, especially mixed paper. Mixed paper is a group of about 60 different paper products, some of which are recyclable and some of which are not. However, it does not include main paper products such as cardboard, newspaper, and magazines. By separating used mix paper into recyclable or non-recyclable paper, it makes possible to recycle. Correct separation is necessary because miss-separation, for example, non-paper materials, or oil stains paper can stop the recycling at plant. On the other hand, mixed paper includes a very wide variety of paper products. Therefore, it is not easy to manually separate recyclable or non-recyclable paper correctly. According to the 2021 survey, in offices, recovered paper collection rate of mixed paper was low at about 50% [2]. In Fukuoka City (in Japan) in 2019, the causes of recovered paper not being separated in offices were investigated [3]. In this study the main causes were "to separate used paper is a burden" "Not enough recovered paper quantity" "There is no place to store recovered paper". One way to increase the collection rate of mixed paper is to reduce the burden by using tools that support separation.

In recent years, with the increased use of Information Technology (IT), the use of such technology has become increasingly active in the waste management. Especially, Artificial Intelligence (AI)-based technologies can be applied in the process of waste separation. Image Recognition AI have also been done. One of

them is object detection, which is used to recognize the position and type of objects in an image when there are many objects in the image. Zhang et al. (2022) used the YOLO algorithm to classify five types of waste: glass, fabric, metal, plastic, and paper, with an accuracy of 93.12% for mAP [4]. YOLO algorithm [5] is a general object detection method and is based on Convolutional Neural Network (CNN), a one of deep learning methods. Qiao et al. (2023) used the same method of classification as above in a low-illumination scenes, and their accuracy was 77.88% for mAP [6]. In particular, study on separating types of paper is below. Vrancken et al. (2019) used deep learning AlexNet to classify images of 24 paper products into two classes, paper and cardboard, with an accuracy of 76.6-77.5% [7]. Mao et al. (2022) performed object detection using the YOLO algorithm for carton, paper containers, metal, glass, plastic, and plastic bottles as household waste products, with an accuracy of 92.12% for mAP [8].

Few studies have used object detection to classify many types of paper products. Therefore, in this study, the YOLO algorithm will be used to classify 12 types of mixed paper to check its accuracy. The purpose of this study is to build a system to support the classification of used papers based on this technology.

#### Methodology

#### YOLO

YOLO, which stands for 'You Only Look Once', used in this study is a popular object detection and image segmentation method. YOLO, proposed by Redman et al. in 2016 [9] has impacted the world of object detection due to its high speed of detection. In comparison to another systems, YOLO makes real-time use of object detection more realistic.

YOLO divides the input image into multiple grid cells and detect bounding boxes that is sub-area surrounding an object. At the same time, probability of the type of object present in each grid cell is calculated. And multiply the trust level of the bounding box by the probability of the type in each cell to determine the position of the object and its type.

#### Target paper type

This study covered commonly used 12 types of paper. Table 1 shows target types of paper and recyclability. Here, this recyclability is based on the rules of Fukuoka City as one example.

#### **Training data**

To do object detection, we first need to train. We create our own data for training. The images of used paper were collected by taking photos using camera, or by downloading paper images from the internet (For example, Fig.1). As the amount of image data was not sufficient, the data was multiplied by cutting out parts of image, changing the color tones, rotating, enlarging, and reducing the size of the image-by-image processing. In addition, background of the image was varied to 14 different types to adapt to a variety of photos. And one image contained only one paper product in training data. As a result, 500 images were created for training per paper class and 6,000 images for all class.

#### Annotation

When creating a dataset for training in object detection, a labeling process called annotation is required. Annotation is an indication of the extent of an object's area in the image, that is bounding box for each paper product. This task was performed using the annotation tool "labeling" [10], which is commonly used in object detection tasks. Annotation was performed by one person.

#### Training

In YOLO, various parameters can be set that determine how training proceeds. The Number of training sessions was set to 300, the size of the input image was set to  $1024 \times 1024$  to match the pixels of the created image, and the learning rate (lr) was set to 0.01, which is the default.

| Table 1 | Target | types | of | paper |
|---------|--------|-------|----|-------|
|---------|--------|-------|----|-------|

|    | paper class         | recyclable or not<br>in Fukuoka City |  |
|----|---------------------|--------------------------------------|--|
| 1  | calendar            | recyclable                           |  |
| 2  | envelope            | recyclable                           |  |
| 3  | juice pack          | non-recyclable                       |  |
| 4  | milk pack           | recyclable                           |  |
| 5  | paper bag           | recyclable                           |  |
| 6  | paper cup           | non-recyclable                       |  |
| 7  | postcard            | recyclable                           |  |
| 8  | receipt             | non-recyclable                       |  |
| 9  | (sales) slip        | non-recyclable                       |  |
| 10 | toilet paper (core) | recyclable                           |  |
| 11 | paper box           | recyclable                           |  |
| 12 | tissue box          | recyclable                           |  |

#### Validation

After the training phase, object detection is performed on image data for verification using the obtained model in training, and its accuracy is evaluated. Verification data included several different paper products in one image. (For example, Fig.2). The reason for this is to verify that this system is all-purpose in many usage scenarios. The amount of validation data ranged from 148 to 483 paper products per class, for a total of 3196 (Table 2).

#### **Evaluation Method**

The results of object detection are divided into four categories: True Positive (TP), False Positive (FP), False Negative (FN) and True Negative (TN). Each of these is classified and illustrated in Table 3. Using the number of cases of TP, FP, and FN in these indices, Precision and Recall can be calculated. Precision is the percentage of correct responses when an object is detected from an image. Recall is the percentage of correct responses when an object exists in the image. Precision and Recall are expressed using TP, FP and FN as follows.

$$Precision = \frac{TP}{TP + FP}$$
$$Recall = \frac{TP}{TP + FN}$$





The with

| Table 2         Validation |           |  |  |
|----------------------------|-----------|--|--|
| class                      | Number of |  |  |
|                            | items     |  |  |
| all                        | 3196      |  |  |
| calendar                   | 226       |  |  |
| envelope                   | 393       |  |  |
| milk pack                  | 396       |  |  |
| paper bag                  | 357       |  |  |
| postcard                   | 287       |  |  |
| toilet paper               | 329       |  |  |
| paper box                  | 433       |  |  |
| tissue box                 | 281       |  |  |
| juice pack                 | 483       |  |  |
| paper cup                  | 292       |  |  |
| receipt                    | 291       |  |  |
| slip                       | 148       |  |  |

curve data

Table 3 4 types of object detection results

| plotted as Precision on the vertical axis and Re   | call | on   |
|--|------|------|
| the horizontal axis is called the Precision Recall | Cur  | rve. |
| AP (Average Precision) is the area bounded         | by   | the  |
| Precision Recall Curve and is expressed            | by   | the  |
| following equation.                                |      |      |

$$AP = \int_0^1 p(r)dr$$

p: Precision

r: Recall

AP is often used as an evaluation metric for object detection, with closer to 1 indicating a better learned model. And mAP is obtained by averaging this AP for all classes. In this study, mAP50 is used as the evaluation index. This variable is the mAP when the IoU (Intersection over Union) that represents the ratio of the area of overlap between the predicted bounding box and the true value bounding box. is bigger than 0.5.

#### RESULTS

Validation results are shown in Table 4 and Fig.3. Table 4 shows the Precision, Recall, and mAP50 values for each class. In Fig.3, the confusion matrix is shown. The confusion matrix represents the actual true class on the horizontal axis and the class detected by YOLO on the vertical axis. The numbers in the figure are the ratio of the number of objects detected by YOLO to the total number of objects in target class.

The validation results for all the classes showed an mAP50 of 0.714 from Table 4. It was shown that object detection for all the classes possible with an average accuracy of 71.4%. The verification results by classes

|          | Predicted class |                        |                        |  |
|----------|-----------------|------------------------|------------------------|--|
|          |                 | А                      | Not A                  |  |
| True cla | А               | True Positive<br>(TP)  | False Negative<br>(FN) |  |
| SS       | Not A           | False Positive<br>(FP) | True Negative<br>(TN)  |  |

Table 4 Results of validation

| class        | Precision | Recall | mAP50 |
|--------------|-----------|--------|-------|
| all          | 0.76      | 0.647  | 0.714 |
| calendar     | 0.819     | 0.783  | 0.816 |
| envelope     | 0.772     | 0.83   | 0.866 |
| milk pack    | 0.691     | 0.505  | 0.616 |
| paper bag    | 0.714     | 0.586  | 0.661 |
| postcard     | 0.888     | 0.652  | 0.713 |
| toilet paper | 0.83      | 0.342  | 0.597 |
| paper box    | 0.542     | 0.741  | 0.619 |
| tissue box   | 0.828     | 0.583  | 0.724 |
| juice pack   | 0.652     | 0.652  | 0.682 |
| paper cup    | 0.585     | 0.336  | 0.427 |
| receipt      | 0.903     | 0.797  | 0.889 |
| slip         | 0.891     | 0.959  | 0.958 |



Fig.3 Confusion matrix (varidation1)

showed that I recision execute 1070 in many classes from Table 4. While Recall was particularly low with toilet paper and paper cups in the 30% range. This indicates that toilet paper and paper cups were without detection. For this cause, Fig.3 shows that 39% of the toilet paper and 42% of the paper cup is detected as background. An example of an image that could not be detected is shown in Fig.4. From this figure, it was thought that the cause was that the features were hidden due to overlapping objects. Another problem was that milk pack and juice pack were mis-detected as paper box in 18% and 15%, respectively. Possible cause of false detection is that milk pack and juice pack are similar in shape, color, and gloss to paper box.

#### CONCLUSION

In conclusion, this study built the used paper separation support system which utilizes image recognition AI (YOLO) and to evaluate its accuracy for 12 types of paper product. The findings obtained from this study are as follows:

- Average in all type of mAP50 which represents the detection accuracy was 0.714, indicating that object detection for all the 12 types of paper product performs an average accuracy of about 71%.
- Two types of factors were founded to reduce accuracy: the first was feature concealment due to overlapping objects in the image; the second was misrecognition due to similarities in the appearance.

From these, we believe that this used paper separating support system have a potential for the practical application.

#### ACKNOWLEDGEMENTS

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Fig. 4 Example of mis-detection due to

#### overoverlapping

## Receiving Performance of a Method of Detecting for Lithium-Ion Batteries(LIBs) by Attaching RFID Tag to the LIBs

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#### ABSTRACT

There have been many incidents of ignition caused by lithium-Ion Batteries (hereinafter referred to as "LIBs") mixed in noncombustible waste and other materials. In this study, we conducted basic research on a method to detect products containing LIBs mixed in waste, based on the premise that RFID (Radio Frequency Identification) tags are attached to LIBs. RFID tags are widely used as automatic identification technology. The tag used in the experiment was a unidirectional RFID tag antenna under development, which has the feature of being able to receive radio waves from a reader/writer (hereafter referred to as R/W) even when attached to a metal product. In this study, the basic performance of the tags was verified and the reception strength and distance of the tags were measured in the presence of obstacles (several types of waste) and under general environmental conditions. The results show that if the distance between the tag and R/W is approximately 2.5 m or less, detection is possible even in the presence of obstacles such as metal. It was also observed that placing the tag in a space surrounded by metal increased the reception strength compared to that of the tag alone. This result suggested the possibility of LIBs detection using unidirectional RFID tag antenna, although there is a limit to the distance between the tag and the R/W.

#### 1. Introduction

In recent years, there have been many incidents of smoke and fire caused by Lithium-Ion Batteries (hereinafter referred to as LIBs) mixed in with noncombustible waste, etc. If LIBs are present at the loading ports of packer trucks or crushing equipment at recycling facilities, they may ignite due to excessive compression or crushing of the LIBs.<sup>1)2)3)4)5)</sup> The fire problem. accident is а serious Currently, countermeasures against such fire accidents include early detection of abnormal temperature rise of waste and smoke/fire and introduction of automatic fire extinguishing systems<sup>6)</sup>, but these are only

post-detection. In order to reliably reduce the number of accidents, it is necessary to take pre-detection and remove LIBs mixed in refuse before it is collected and processed. Recently, a technique has been studied to measure the concentration of dimethylcarbonate leaking from the LIBs using two-wavelength optical absorption spectroscopy.<sup>7)</sup> Dimethylcarbonate is used as an electrolyte in LIBs, and its explosion limit is between 4.2 and 12.9%. The objective of the study is to detect concentrations below 4.2%, which is the lower bound of the explosion limit. While this technology can detect the presence of LIBs that have leaked gas due to crushing, etc. It cannot detect the presence of LIBs in advance in a state before gas is generated.

Our study aims to construct a LIBs detection system that can be implemented in society, based on the premise that RFID (Radio Frequency Identification) tags attached to LIBs. Since general FRID tags cannot transmit radio waves when attached to metal products such as LIBs, this study used RFID tags under development at Kyushu University.

We have confirmed in an anechoic chamber that the RFID tag works properly when attached to a LIBs, and clarified the relationship between the reception strength depending on the distance between the tag and the reader/writer (hereinafter referred to as R/W) and the tag's orientation. Furthermore, for the purpose of practical application of this detection system, tag reading experiments were conducted when tags were placed not only in an anechoic room but also in a general living environment to confirm the effect on reception.

#### 2. Materials and methods

#### 2.1 RFID tags

Two types of RFID tags were used in the experiment. One is a unidirectional RFID tag antenna operating in the 900 MHz band developed by Kanaya et al.<sup>8)9)</sup> (called an A-tag), and the other is a commonly used general RFID tag antenna used for clothing price tags (called a B-tag). In the case of B-tags, if the tag is in contact with metal or liquid, the reflected waves from the antenna are canceled out or absorbed. This makes reception difficult by the reader/writer (hereafter referred to as R/W, DENSO WAVE UHF band RFtag high-power handy scanner SP1) which transmits radio waves to the tag and receives the reflected waves from the tag. On the other hand, A-tag have "unidirectional performance" meaning that radio waves do not propagate in the direction of the tag's installation surface. Therefore, A-tag can successfully reflect radio waves in the direction opposite to the metal surface (R/W direction) even if it is in contact with the metal surface. The layout of the two types of A-tags (large type and small type) is shown in Figure 1.

#### 2.2 Experimental Methods

An overview of the experimental equipment is shown in Figure 2. The experiment was conducted in an anechoic chamber, where the entire room was lined with radio wave absorber that block the effects of external radio waves in order to eliminate the influence of radio waves present in the general environment.

The R/W and the tag were placed at the same height. Received strength was measured by changing the distance between the tag and the R/W and by changing the reception angle by rotating the tag clockwise and counterclockwise. Reception strength is indicated by the received signal strength indicator (RSSI) value. The higher the RSSI value, the more stable the reception.

The reception strength in each experiment was the average of RSSI values (dBm) measured 10 times consecutively. Reception strength and reception range are shown in the radar chart. Reception range is shown from 0 to 180 degrees clockwise and from -180 to 0 degrees counterclockwise.

(1) Confirmation of the unidirectional performance of A-tag

To confirm the unidirectional performance of A-tag, a comparison was made with B-tag in terms of reception performance. Reception measurements were made in two cases, one with the tag alone and the other with A-tag and B-tag attached to the mobile battery.(Figure 3)









Figure 2 Experiments in an anechoic chamber



Figure 3 The tag attached to the mobile battery

The mobile battery has a metal casing and LIBs inside, and is the biggest cause of fires caused by rechargeable batteries.<sup>10</sup>

(2) Confirmation of reception status in general environment

In addition to the previous measurements in an anechoic chamber, the detection was also checked in a general environment where other radio waves, such as Wi-Fi, were present. We chose laboratories, corridors, and outdoor plaza on the university campus. The distance between the tag and R/W was set at 5 m, the maximum reception distance for A-tags, and varied in three steps.

(3) Confirmation of the effect of a metal cylinder on reception conditions

In one of the experiments described in (2) above, in the corridors, the results showed that the tag could be detected from all directions to the tag. In the case of A-tag, it can normally be detected only in the direction that the tag and R/W are facing(front side), but in the case of the corridors, the tag could be read from the back side of the tag as well as from the front side. As a factor, we thought that a space surrounded by metal, such as a corridor made of reinforced concrete, would expand the detection range. Therefore, we conducted further research into the effect of spaces surrounded by metal on the reception of the tag. We prepared a metal cylinder (material: galvanized steel sheet, size:  $\Phi$  600 mm x L900 mm) and a garbage bag filled with about 20 empty cans with a mobile battery that attached A-tag(small type). The garbage was installed inside the cylinder as shown in Figure 4. We compared the reception status of A-tag between the case where the garbage bag was placed inside the metal cylinder and for the case where the garbage bag alone. Furthermore, the electrolytic field strength in the inside space of the cylinder and on the surface of the tag was quantified by simulation.

#### 3. Results and discussions

Results and discussion are presented for each experimental item.

3.1 Confirmation of the unidirectional performance of A-tag (large type)

We affixed A and B tags to a mobile battery and compared the results with those obtained with the tag alone. When A-tag was affixed to the mobile battery, the reception strength of A-tag was equal to or greater than that of A-tag alone, but when B-tag was affixed to the mobile battery, it could not be received. This confirmed the unidirectional performance of A-tag.(Figure 5)

3.2 Confirmation of reception status in general environment

Based on the results in the anechoic room, the same method was used to check reception in general environments where WiFi radio waves are present or metal products are nearby. The results are shown in Figure 6.



Figure 4 Experiments in using metal cylinder

In the laboratory, the maximum reading distance was only 1.9 m. However, at a distance of 1 m, the maximum reading range was  $\pm 90$  degrees, as in the anechoic chamber. At a reception distance of 1 m, the counterclockwise (-90 to 0 degrees) reception strength was 4 to 8 dBm greater than the clockwise (0 to 90 degrees). The reason why the counterclockwise direction was easier to read is that there is a partition in this direction, we expect that the metal inside the partition affected the reception.

In the corridor, the results of reception conditions were equivalent to those in the anechoic chamber. Furthermore, even when the tag was set at a reception distance of 2.5m and 1m, and the tag was facing backward, it could be read within a range of  $\pm 90$  to  $\pm 180$  degrees. This result was not confirmed even in experiments in an anechoic chamber. We thought that this might be due to the fact that the corridor floors and walls are made of reinforced concrete. We assumed that the R/W received radio waves from all angles because the metal inside the reinforced concrete reflected radio waves in various directions.

Finally, outdoors, the reception distance was only up to 4 m, but at 2.5 m and 1 m, the reception results were equivalent to those in an anechoic chamber.



Figure 5 Comparison of RSSI and reception range of A and B-tag between tag alone and tag affixed to mobile battery



Figure 6 Comparison of RSSI and reception range under general environment

3.3 Confirmation of the effect of a metal cylinder on reception conditions

The results are shown in Figure 7. When a garbage bag alone, the receiving distance could only be read up to 1 m. On the other hand, when the garbage bag was placed inside the metal cylinder, it could read up to 1.5 m. As for the reception strength, when the garbage bag was placed inside the metal cylinder, it was about 30 dBm greater than when a garbage bag alone.



Figure 7 Comparison of RSSI and distance A-tag placed inside the metal cylinder and A-tag alone

Shows the results of analyzing the electric field strength of around the garbage bag and the surface of the tag. Comparing the electrolytic field strength around the garbage bag when the bag placed alone and inside the metal cylinder, the values for the garbage bag alone was generally 10 to 20 V/m, while that for the garbage bag inside the metal cylinder was generally 50 to 140 V/m, indicating higher values. (Figure 8) The maximum electric field strength on the surface of the tag was about 25 V/m when a garbage bag alone, but when the the garbage was placed in the metal cylinder, the maximum electric field strength was about 375 V/m. (Figure 9) Since the electric power is proportional to the square of the electric field strength, the difference in received electric power is obtained by equation (1).

Received electric power difference (dB)  
== 20 
$$\log_{10} \frac{E_2}{E_1}$$
 (1)

Here,  $E_1$  (=25V/m)is the electric field strength when a garbage bag alone and  $E_2$  (=375V/m)is the electric field strength when a garbage bag was placed in the metal cylinder.

Calculations using equation (1) show that the received electric power is 23.5 dBm greater when the garbage bag was placed in a metal cylinder than when the garbage bag alone.

The reason why the reception strength increased by placing the garbage bag inside the metal cylinder is thought to be because the metal cylinder suppressed the diffusion of radio waves.



Figure 8 Comparison of electric field strength of around the garbage bag



Figure 9 Comparison of electric field strength of the surface of A-tag

#### 4. Conclusion

The purpose of this study is to construct a system to detect LIBs containing products mixed in waste by attaching the unidirectional RFID tag antenna to LIBs. Using the tag which under development, measurements of reception status of the tag in various situations were conducted. As a result, the following findings were obtained.

- (1) Due to the unidirectional performance of the tag, the tag could be detected even if it was attached to a product containing metal objects that weaken radio waves, such as a mobile battery.
- (2) Even in general environments where other radio waves such as Wi-Fi exist, reception performance equivalent to that in an anechoic chamber was confirmed at a reception distance of 1 m or less in the laboratory and 2.5 m or less outdoors. On the other hand, in a corridor, reception was confirmed to be possible in all 360° directions.
- (3) It was confirmed that placing the tag in a space surrounded by metal increased the reception strength compared to that of the tag alone. Simulation results of the electric field strength under this experimental condition also confirmed that the received electric power was 23.5 dBm higher when the tag was placed on the metal cylinder than when the tag was placed alone.

These results show that if attaching a unidirectional RFID tag antenna to LIBs is implemented in society, it will be possible to detect LIBs mixed in with various types of waste by waste collection workers handling W/R or installing R/W on packer trucks. This will make it possible to prevent fires caused by LIBs in advance. In addition, since LIBs can be collected in their original form, this will also contribute to recycling of LIBs.

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# Distribution of copper and gold in bottom ash from municipal solid waste incineration based on particle size and waste input

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#### Abstract

This study examines the concentrations and distributions of copper (Cu) and gold (Au) in bottom ash from three municipal solid waste incinerators (MSWI) in Japan. The results reveal that mass distribution in all samples peaks in the 0.5-2 mm fraction, with over 70% of particles <4 mm. Cu concentration initially increases and then decreases with particle size increasing, peaking at >20,000 mg/kg in the 2-4 mm fraction. Over 94% of Cu is found in fractions >0.5 mm. Bottom ash A meets recovery criteria across all fractions (except <0.5 mm), while only the 2-4 mm fraction of bottom ash B meets these standards, and all fractions >2 mm in bottom ash C meet the criteria. Average Cu concentrations are: bottom ash A (15,783.03 mg/kg), bottom ash C (7,749.71 mg/kg), and bottom ash B (7,372.15 mg/kg), all meeting recovery criteria. For Au, concentrations follow a similar trend, peaking at 13.95 g/t in the 2-4 mm fraction of bottom ash A, 7.93 g/t in bottom ash B, and 7.55 g/t in bottom ash C. Over 86% of Au in bottom ash A and B is in fractions >0.5 mm, while about 95% in bottom ash C is in fractions <4 mm. All fractions meet recovery standards. Average Au concentrations are: bottom ash A (12.37 g/t), bottom ash B (6.68 g/t), and bottom ash C (5.70 g/t), all meeting recovery standards. The study highlights how particle size and waste input influence the distribution of Cu and Au in bottom ash, offering insights for sustainable and cost-effective waste management.

Keywords: Bottom ash, Copper, Gold, Particle size, Waste input.

#### 1. Introduction

With population growth and improving living standards, the generation of municipal solid waste (MSW) has been increasing annually. According to a World Bank report and related studies, global MSW production reached 2.24 billion tons in 2020 and is projected to rise to 3.88 billion tons by 2050 (Y. Zhang et al. 2021; Kaza, S., 2018; World Bank, 2022.) . Municipal solid waste incineration (MSWI) effectively reduces the volume, mass, and organic content of MSW while also recovering energy, making it a preferred waste management method in many countries. In Japan, incineration is the dominant waste disposal method, with 80% of MSW processed through incineration in 2020 (Ministry of the Environment, Japan. 2022). That year, Japan operated 1,056 incinerators, handling 33.466 million tons of waste. Similarly, in China, the adoption of MSWI has grown significantly, with approximately 80% of MSW incinerated in 2022, totaling 195.021 million tons (National Burea of Statistics, China. 2022). The incineration process generates a substantial amount of solid residues, including bottom ash and fly ash, with bottom ash accounting for 80 - 95% of the total ash weight (Y. Zhang et al. 2021; Sun and Yi 2021; Hu et al. 2021). Bottom ash primarily consists of minerals (50-70%), glass and ceramics (10-30%), unburned materials (15%), ferrous metal particles (5-15%), and non-ferrous metal particles (1-5%) (Šyc et al. 2020). Typically, bottom ash is either landfilled or utilized as an additive in construction materials, such as road base layers (Zhao et al. 2023). However, bottom ash contains significant concentrations of heavy metals, including Cu, Pb, Zn, As, Ni, and Cr, which pose potential risks to both the environment and human health (J. Yao et al. 2010; H. Zhang, He, and Shao 2008; Back and Sakanakura 2021). Additionally, bottom ash contains rare earth elements (e.g., Ce, Nd, La, Y, Lu) (Beikmohammadi et al. 2023; O. Yao et al. 2014) and precious metals (e.g., Au, Ag) (Beikmohammadi et al. 2023; Abramov et al. 2022). Therefore, directly landfilling bottom ash or using it in construction materials results in resource loss and undermines the environmental sustainability of waste incineration.

In recent years, with the depletion of natural mineral resources, attention has shifted towards end-of-life products, or waste, often referred to as "urban mines." Among these, MSWI bottom ash has garnered significant interest. Much of the research has focused on investigating the concentrations of heavy metals, precious metals, and rare earth elements across different particle sizes in bottom ash. For instance, studies have found that approximately 70% of Cu is

concentrated in particles<7mm (Böni, M.L., 2013), while significant amounts of precious metals such as gold and silver are typically found in particles >2mm (Muchova, Bakker, and Rem 2009; Allegrini et al. 2014; Holm and Simon 2017). However, other research has revealed that the 0.5 - 2.0mm fraction contains the highest Au concentration, averaging 28.82 ± 1.62 mg/kg (Abramov et al. 2022). Additionally, some studies report that the average concentrations of heavy metals (e.g., Zn, Cu, Pb, Cr) in bottom ash tend to be higher in particles <4mm, with Au and Ag levels particularly elevated in particles <0.5mm (Beikmohammadi et al. 2023). Thus, the resource content in bottom ash varies not only by particle size but also by its source. Since the composition of waste input plays a critical role in determining the presence and quality of resources in bottom ash (Biganzoli et al. 2012; Hu et al. 2011; Astrup, Riber, and Pedersen 2011), and given that waste composition differs between regions due to factors such as geography, seasonality, lifestyle, and waste sorting practices, the composition of bottom ash also varies across different locations. Moreover, several other factors, including furnace design, combustion temperature, and quenching process, can influence the composition of bottom ash (Nakić et al. 2021; Vasarevičius, Seniūnaitė, and Vaišis 2022).

Since the resource content in bottom ash varies with particle size and the composition of waste input, it is essential to investigate the distribution of resources in specific bottom ash samples before resource recovery. This study focuses on Cu, a representative heavy metal with high market value and significant concentration in bottom ash, and Au, a representative precious metal. The research examines the content and distribution of Cu and Au across different particle sizes in bottom ash from three MSWI facilities in Japan. The findings aim to provide a theoretical basis for the recovery of metal resources from bottom ash and to explore new opportunities for sustainable and cost-effective waste management.

#### 2. Materials and method

#### 2.1 Sampling and sample preparation

The bottom ash samples for this study were collected from three different incineration plants (A, B, and C) in Japan. Plants A and B are located in the same city, while Plant C is situated in a different city. The composition of waste input for these incineration plants is illustrated in Fig. 1. It is worth noting that coarse particles had been removed from the bottom ash prior to sampling.

3 kg of bottom ash was collected from each of the three sources (A, B, and C) and subjected to sieving experiments based on particle size ranges: <0.5 mm, 0.5-2 mm, 2-4 mm, and >4 mm. For each bottom ash sample, 1 kg was sieved per experiment, with the process repeated three times. This resulted in three parallel samples for each particle size fraction, yielding a total of 36 samples. The sieved bottom ash samples were then dried in an oven at  $105^{\circ}$ C for 24 hours. After drying, the samples were weighed and sealed in plastic bags for storage.



Fig. 1 The composition of waste input for these incineration plants.

#### 2.2 Elemental analysis

The major elemental composition of milled samples was determined using Energy Dispersive X-ray Fluorescence Analysis (ED-XRF), employing a Spectro Xepos spectrometer with matrix-adjusted calibration. The measurements were conducted on pressed powder pellets with a diameter of 32 mm.

To determine the content of Cu and Au, the samples were digested with aqua regia. The digests were analyzed by Inductively Coupled Plasma Spectroscopy (ICP-OES).

#### 3. Results and discussion

#### 3.1 Particle size distribution

The mass distribution of bottom ash by particle size is presented in Fig. 2, showing that the particle size distribution varies across the different bottom ash samples. Studies have shown that the particle size distribution of bottom ash can differ based on factors such as location, time, waste input, air-to-MSW ratio, and the degree of mixing within the incineration furnace (Zhu et al. 2020; Chang and Wey 2006). As a result, the percentage of particles in each size fraction differs among the bottom ash samples. Despite these variations, some commonalities can still be identified. In all three bottom ash samples, the mass distribution peaks within the 0.5-2 mm particle size range, and over 70% of the total bottom ash consists of particles <4 mm. This finding aligns with previous studies (Back and Sakanakura 2021). Additionally, a bimodal distribution is observed in the particle size distribution of bottom ash B, as shown in Fig. 2. One peak occurs in the 0.5-2 mm range, while another is found in the >4 mm range. Previous research suggests that such bimodal distributions in incineration ash may result from sampling at multiple points within the incineration plant (JANKOWSKI et al. 2006; Koukouzas, Ketikidis, and Itskos 2011; Li et al. 2012).

#### 3.2 Major elemental composition in bottom ash

The major elements concentration (>1g/100g) of bottom ash samples by XRF is presented in Table 1. The results indicate that calcium (Ca) and silicon (Si) are the most abundant elements, collectively accounting for over 50% of the mass fractions, with variations depending on particle size. Studies suggest that the high Ca content may originate from construction materials present during the incineration process (Q. Yao et al. 2014). However, there is no construction materials in the waste inputs of the three incineration plants. This suggests that the elevated Ca levels likely come from combustible waste, particularly kitchen waste, such as fish bones. Table 1 also reveals the presence of heavy metals, including aluminum (Al), iron (Fe), zinc (Zn), and copper (Cu), in the bottom ash. Although coarse particles in the bottom ash were removed prior to

sampling, some visible metal particles remained. During the preparation of XRF samples, these visible metal particles were picked out, as their ductility makes them difficult to grind. Therefore, the heavy metal concentrations in Table 1 primarily reflect metals that have melted and adhered to the ash during incineration, as well as those present in very fine metallic particles. Additionally, Table 1 shows that larger particle sizes are associated with higher relative standard deviations (RSD). This is attributed to the increased heterogeneity of the material as particle size grows. In addition, random errors during the sampling process also contribute to the high RSD.



**Fig. 2** Mass distribution of bottom ash by particle size: (a) bottom ash A, (b) bottom ash B, (c) bottom ash C.

| Element | Bottom ash A |             |                   | Bottom ash B |             |             |              | Bottom ash C |             |              |                   |              |
|---------|--------------|-------------|-------------------|--------------|-------------|-------------|--------------|--------------|-------------|--------------|-------------------|--------------|
|         | <0.5mm       | 0.5mm-2mm   | 2mm-4mm           | >4mm         | <0.5mm      | 0.5mm-2mm   | 2mm-4mm      | >4mm         | <0.5mm      | 0.5mm-2mm    | 2mm-4mm           | >4mm         |
| Ca      | 47.47±1.11%  | 40.33±3.05% | 39.14±3.12%       | 39.94±3.36%  | 52.80±2.43% | 47.98±0.82% | 39.14±2.06%  | 33.61±4.90%  | 53.16±2.03% | 35.54±1.64%  | 22.57±2.89%       | 17.15±18.35% |
| Si      | 14.51±2.75%  | 21.53±5.44% | 22.40±3.59%       | 21.15±3.61%  | 9.97±4.16%  | 15.41±0.19% | 21.36±2.38%  | 29.45±6.40%  | 11.35±6.76% | 24.98±3.31%  | 35.49±0.77%       | 34.30±7.43%  |
| Al      | 7.81±1.51%   | 9.30±4.88%  | 9.34±0.95%        | 9.44±6.71%   | 7.94±6.95%  | 7.20±0.81%  | 8.03±0.21%   | 9.59±6.79%   | 14.94±0.83% | 13.97±0.62%  | 13.44±1.49%       | 12.25±8.19%  |
| Cl      | 7.39±1.71%   | 6.50±4.36%  | 6.21±3.39%        | 6.39±4.60%   | 8.31±1.84%  | 6.60±0.45%  | 5.48±1.88%   | 3.93±11.89%  | 3.44±2.50%  | 2.01±4.81%   | 1.22±6.56%        | 0.78±17.62%* |
| Fe      | 4.36±3.19%   | 5.01±2.38%  | 5.33±6.27%        | 5.62±6.01%   | 7.23±3.73%  | 9.02±2.99%  | 11.90±9.35%  | 10.13±7.92%  | 5.11±5.08%  | 7.79±2.28%   | 11.41±3.38%       | 17.88±5.16%  |
| Ti      | 2.84±0.92%   | 2.51±1.46%  | 2.48±4.03%        | 2.48±3.75%   | 2.22±2.08%  | 2.10±1.02%  | 1.87±0.27%   | 2.18±39.93%  | 1.68±3.83%  | 1.95±2.78%   | $1.31 \pm 1.77\%$ | 0.89±23.57%* |
| Κ       | 2.42±0.61%   | 2.97±1.44%  | 2.97±0.57%        | 2.79±2.99%   | 1.97±1.27%  | 2.09±0.54%  | 2.21±2.70%   | 2.20±3.08%   | 1.72±3.05%  | 3.15±0.23%   | 3.33±1.44%        | 2.35±7.15%   |
| S       | 2.31±2.80%   | 2.04±7.12%  | 2.02±4.09%        | 2.19±3.84%   | 2.06±4.40%  | 1.65±0.43%  | 1.31±4.60%   | 0.81±11.88%* | 0.40±3.36%* | 0.26±5.28%*  | 0.18±6.18%*       | 0.18±19.71%* |
| Na      | 2.20±4.26%   | 2.62±2.84%  | 2.61±5.13%        | 2.53±4.68%   | 2.03±0.71%  | 2.19±1.03%  | 2.54±1.70%   | 3.50±3.45%   | 2.16±1.22%  | 3.05±1.20%   | 3.21±3.87%        | 2.65±26.32%  |
| Zn      | 2.18±1.14%   | 1.34±4.38%  | 1.52±19.55%       | 1.64±14.83%  | 1.06±2.38%  | 0.93±6.48%* | 0.85±12.47%* | 0.71±49.02%* | 1.13±1.57%  | 1.19±6.12%   | 1.04±22.39%       | 2.62±104.21% |
| Mg      | 1.79±0.19%   | 1.59±1.42%  | 1.63±0.81%        | 1.62±1.31%   | 1.49±0.75%  | 1.63±0.89%  | 1.65±1.39%   | 1.50±5.25%   | 1.37±2.59%  | 1.69±1.71%   | $1.81 \pm 2.70\%$ | 2.14±2.20%   |
| Р       | 1.67±1.96%   | 1.51±2.24%  | $1.41 \pm 1.70\%$ | 1.34±3.20%   | 1.37±4.14%  | 1.62±0.09%  | 1.78±4.73%   | 1.32±10.33%  | 2.31±2.92%  | 2.98±1.42%   | 3.09±9.73%        | 1.63±26.66%  |
| Cu      | 1.21±3.72%   | 1.10±7.92%  | 1.13±9.19%        | 1.08±20.25%  | 0.37±2.63%* | 0.42±3.95%* | 0.71±23.73%* | 0.27±14.62%* | 0.27±7.60%* | 0.38±25.50%* | 0.43±41.65%*      | 0.64±26.94%* |

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| Table 1 Major elements concentration (> 1g/100g) of bottom ash samples by XRF. Average values reported in 1g/100g with relative standard devi | ation. |
|---|--------|
|---|--------|

\*The element concentration is below 1g/100g

## **3.3** Copper and gold distribution in various bottom ash and particle sizes

To evaluate whether the Cu and Au contents in bottom ash meet the recovery criteria, this study refers to the Chinese geological and mineral industry standards, as well as ore concentration levels cited in other studies, as summarized in Table 2.

| Table 2 | Criteria | for the | recoverability | of | Cu an | d Au |
|---------|----------|---------|----------------|----|-------|------|
|         |          |         |                |    |       |      |

|        | Criteria               |                             |                                    |  |  |  |
|--------|------------------------|-----------------------------|------------------------------------|--|--|--|
| Metals | Cut-off<br>grade       | Minimum<br>industrial grade | Ore<br>concentration<br>min-max    |  |  |  |
| Cu     | 0.5 (wt%) <sup>a</sup> | 0.7 (wt%) <sup>a</sup>      | 5000-20000<br>(mg/kg) <sup>b</sup> |  |  |  |
| Au     | 0.5 (g/t) <sup>a</sup> | 2.0 (g/t) <sup>a</sup>      | <5-30 (g/t) <sup>c</sup>           |  |  |  |

<sup>a</sup>: (DZ T0214-2020).

<sup>b</sup>: (Schlesinger, M.E., Biswas, A.K., 2011).

<sup>c</sup>: (Kongolo and Mwema 1998).

Fig. 3 shows Cu content in individual size fractions of the bottom ash samples and the mass distribution of Cu across different particle sizes. For Cu, in the three bottom ashes, the Cu concentration increases and then decreases with the increase in particle size. The Cu concentration reaches its highest in the 2-4 mm fraction, with concentrations >20,000 mg/kg. Particle size distribution is a key physical parameter of ash, as it increases heavy metal concentrations when the particle size decreases due to the larger surface area (Wan et al. 2018). However, in this study, over 94% of the Cu is distributed in fractions >0.5 mm. This may be due to copper's low volatility, with copper-containing waste components, such as copper wires and metal pieces, entering the bottom ash during incineration. These components then remain in the larger particle size

fractions. Therefore, the particle size distribution of ash is particularly important (Wan et al. 2018). Although the Cu distribution in the three different bottom ashes is generally similar, some differences exist. As shown in Fig. 3 and Table 2, the Cu concentration in all practical size fractions of bottom ash A meets the cut-off grade (0.5%), minimum industrial grade (0.7%), and the ore concentration range (5,000 mg/kg - 20,000 mg/kg) (except for the <0.5 mm fraction), indicating its potential for recovery. For bottom ash B, only the 2-4 mm fraction has a Cu concentration that meets the cut-off grade (0.5%), minimum industrial grade (0.7%), and the ore concentration (5,000 mg/kg - 20,000 mg/kg). As for bottom ash C, the Cu concentration in fractions >2 mm meets the cut-off grade (0.5%), minimum industrial grade (0.7%), and the ore concentration (5,000 mg/kg - 20,000 mg/kg). In addition, the average Cu concentrations in the three bottom ashes differ significantly, in the following order: bottom ash A (15,783.03 mg/kg), bottom ash C (7,749.71 mg/kg), and bottom ash B (7,372.15 mg/kg), all of which meet the recovery criteria mentioned above. This is mainly because the waste input for bottom ash A includes not only combustible waste but also bulky waste and non-combustible containing metals. Although the latter two types of waste undergo shredding and sorting, previous research in our lab has shown that approximately 10% of the metals still enter the incineration furnace. For bottom ash C, in comparison with bottom ash B, the waste input also includes combustible waste (household and business waste) as well as bulky waste and agricultural waste, particularly metals from bulky waste, which may explain the higher average Cu concentration in bottom ash C compared to bottom ash B. This also demonstrates that waste input significantly affects the composition of bottom ash.





**Fig.3** Cu content in individual size fractions of the bottom ash samples and the mass distribution of Cu across different particle sizes: (a) bottom ash A, (b) bottom ash B, (c) bottom ash C.

Au content in individual size fractions of the bottom ash samples and the mass distribution of Au across different particle sizes are shown in Fig.4. For Au, in the three bottom ashes, the Au concentration increases and then decreases with the increase in particle size. The high Au concentration in bottom ash A is observed in the 2-4 mm and >4 mm fractions, with the 2-4 mm fraction having the highest value of 13.95 g/t, slightly higher than the >4 mm fraction at 13.87 g/t. In the <2mm fractions of bottom ash A, the Au concentration is around 10 g/t. For bottom ash B, the high Au concentration occurs in the 0.5-2 mm and 2-4 mm fractions, with the 0.5-2 mm fraction having the highest value of 7.93 g/t, slightly exceeding the 2-4 mm fraction at 7.14 g/t. In contrast, the <0.5 mm and >4 mm fractions have relatively low Au concentrations, around 5 g/t. The highest Au concentration in bottom ash C is found in the 2-4 mm fraction at 7.55 g/t, while the Au concentration in other size fractions is around 5 g/t. As shown in the figure, over 86% of Au in both bottom ash A and bottom ash B is distributed in fractions >0.5 mm, whereas approximately 95% of Au in bottom ash C is distributed in fractions <4 mm. This indicates that particle size and waste input significantly

affect the distribution of Au in bottom ash. However, despite the varying Au concentrations across different size fractions in the three bottom ashes, all fractions meet the Au cut-off grade (0.5 g/t), minimum industrial grade (1 g/t), and ore concentration range (<5 g/t to 30 g/t), demonstrating their recovery potential. Additionally, the average Au concentrations in the three bottom ashes differ significantly due to variations in waste input, in the following order: bottom ash A (12.37 g/t), bottom ash B (6.68 g/t), and bottom ash C (5.70 g/t), all of which meet the recovery criteria. Apart from metal particles in the waste input serving as a source of Au, studies have shown that combustible waste contains a large amount of items like ink cartridges, earphones, and IC cards, which have a certain amount of gold (Murakami, Jinryo, Yamamoto, Hisahisa., 2018). This also explains why bottom ash A has the highest Au concentration and why bottom ash B, derived solely from combustible waste (household and business waste), still contains a relatively high Au concentration. Furthermore, the figure shows that as particle size increases, the relative standard deviation (RSD) also rises. The reasons for this trend have been explained in detail in Section 3.2

and will not be elaborated on here ...



**Fig. 4** Au content in individual size fractions of the bottom ash samples and the mass distribution of Au across different particle sizes: (a) bottom ash A, (b) bottom ash B, (c) bottom ash C.

#### 4. Conclusion

As municipal solid waste (MSW) generation continues to rise, incineration has become the primary waste disposal method due to its advantages. However, it also produces significant residues, such as bottom ash, which contains high levels of heavy and precious metals. With the depletion of natural resources, bottom ash has gained attention as an unconventional source of these valuable materials. This study analyzes the concentrations and distributions of Cu and Au in different particle size fractions of bottom ash from three municipal solid waste incinerators (MSWI) in Japan, aiming to provide a theoretical basis for metal resource recovery and promote sustainable, cost-effective waste management. The main results are as follows:

The mass distribution across different particle size fractions varies among the bottom ash samples. However, in all three samples, the mass distribution peaks in the 0.5 - 2 mm range, with over 70% of particles being <4 mm. Additionally, the particle size distribution of bottom ash B follows a bi-modal pattern. Ca and Si are the two most abundant elements and contribute more than 50% of the mass fractions, varying with particle size.

The Cu concentration in the three bottom ashes first increases and then decreases with particle size, peaking in the 2–4 mm fraction (>20,000 mg/kg). Over 94% of Cu is in fractions >0.5 mm. Bottom ash A meets the cut-off grade, minimum industrial grade (except <0.5 mm), and ore concentration in all fractions. Only the 2–4 mm fraction of bottom ash B meets these criteria, while all fractions >2 mm in bottom ash C meet the standards. The average Cu concentrations are: bottom ash A (15,783.03 mg/kg), bottom ash C (7,749.71 mg/kg), and bottom ash B (7,372.15 mg/kg), all meeting recovery criteria.

The Au concentration in the three types of bottom ash initially increases and then decreases with particle size. The highest Au concentration in bottom ash A is 13.95 g/t in the 2–4 mm fraction. In bottom ash B, the peak is 7.93 g/t in the 0.5–2 mm fraction, while in bottom ash C, it is 7.55 g/t in the 2–4 mm fraction. Over 86% of Au in bottom ash A and B is in fractions >0.5 mm, while around 95% of Au in bottom ash C is in fractions <4 mm. All fractions meet the cut-off grade, minimum industrial grade, and ore concentration standards. The average Au concentrations are: bottom ash A (12.37 g/t), bottom ash B (6.68 g/t), and bottom ash C (5.70 g/t), all meeting recovery standards.

The particle size and waste input clearly influence the content and distribution of Cu and Au in bottom ash.

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# Effect of pH regulation on lactic acid production by electro-fermentation of food waste

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#### ABSTRACT

The use of food waste (FW) for fermentation to produce lactic acid has a promising future, but the current problems are the difficult operation of substrate mixing fermentation and the low efficiency of lactic acid production. In this study, food waste was used as a fermentation substrate, the method single of electro-fermentation (EF) was used for lactic acid fermentation, and the pH of the system was adjusted to improve the fermentation effect. The results show that electro-fermentation can promote the production of lactic acid, and the lactic acid concentration is the highest when the voltage is applied at 1V, which is 39.7% higher than that of the control group. In addition, the voltage can also improve the activity of key enzymes in the process of glucose metabolism to produce lactic acid. Adjusting the pH of the system to 7.0 every 12h is the best method, which significantly enrich the acid-producing functional microorganisms, optimizes the microbial community structure, and improves the efficiency of lactic acid fermentation.

#### **INTRODUCTION**

Food waste has serious safety risks, so it is necessary to deal with food waste in a timely and effective manner. The use of anaerobic fermentation method to treat food waste can not only realize the treatment of organic waste, but also produce value-added chemicals. Lactic acid is an important organic acid with high economic value. It is feasible to use food waste as lactic acid fermentation substrate for non-aseptic fermentation, and the fermentation cost can be greatly reduced. Microbial electrolytic cell (MEC) can promote the life activities of bacteria such as electroactive microorganisms, accelerate the dissolution of substrates, and help stabilize the structure of microbial community. Studies have been conducted in the directions of methane production and hydrogen production, and good results have been shown. In addition, in the process of lactic acid production by electric fermentation, the influence of fermentation factors on the effect of electric fermentation should also be considered. Among them, pH is an important

influencing factor. pH will affect the enzymatic hydrolysis of fermentable components in the substrate, microbial community structure, product composition and so on, thus affecting the effect of lactic acid fermentation.

In this study, the electrification conditions of electric fermentation were optimized, and then the pH regulation frequency and pH value were optimized for pH, which was an important factor, and the microbial community structure and metabolic process were studied. This paper provides some reference for the research on the production of lactic acid by electric fermentation of food waste.

#### MATERIALS AND METHODS

The food waste used in this research was collected from a student canteen of University of Science and Technology Beijing. After collection, impurities such as large bones, plastics, and glass, which are not conducive to breaking and fermentation, were sorted out first. Then, a pulp mill was used to make the sorted food waste into a slurry, which was divided into sealed bags and stored in an environment of  $-20^{\circ}$ C. Remove the food waste from the refrigerator before use, thaw it at room temperature (25±3 °C), add deionized water at the rate of 1:1(w/w), mix it well and leave it for use without any other treatment.



As shown in Figure 1, the reactor used in this study was a H-type two-chamber electrolytic cell with a single chamber volume of 250ml. The carbon cloth electrode is connected to the negative electrode of the power supply, and the carbon brush electrode is connected to the positive electrode of the power supply. The middle of the cell is separated by a cation exchange membrane. Kitchen waste slurry was added to the cathode chamber and a stirring device was set up. Na<sub>2</sub>SO<sub>4</sub> was added to the anode chamber as an electrolyte solution. The system is provided with constant voltage by a stabilized power supply.

The effects of different applied voltages, the effect of pH adjustment frequency and pH values on electro-fermentation were studied. The organic composition, electrochemical characteristics and microbial community in fermentation solution were determined and analyzed.

#### **RESULTS AND DISCUSSIONS**

#### <u>Selection of applied voltage for electro-fermentation</u> of food waste

In this experiment, the crushed food waste was added to five electrolytic cells respectively, and constant voltage 0, 0.5, 1.0, 1.5, 2.0V (referred to as control group, 0.5V group, 1.0V group, 1.5V group, 2.0V group) was applied respectively. The fermentation was carried out under the condition of no adjustment of pH and no lactic acid bacteria. The concentration changes of lactic acid produced by electro-fermentation were shown in Figure 2.



Figure2 Lactic acid fermentation at different voltages The growth trend of the five experimental groups was similar 72h before fermentation, among which the concentration of V-1.0 group was the highest, while the concentration of V-0.5 group was the lowest, even lower than that of the control group. After 72h, the lactate concentration in the V-0.5 group and the control group began to decrease gradually, while the remaining three groups still increased slightly. In the whole fermentation cycle, the maximum lactic acid concentration from high to low order is: V-1.0 (13.14 g/L) > V-1.5 (12.06 g/L) >V-2.0 (11.28 g/L) >Control (9.41g/L)  $\approx$  V-0.5 (8.77g/L). Compared with the

control group, the lactic acid yield of electro-fermentation under low voltage was increased, and the maximum lactic acid concentration of the experimental group with V-1.0 was the highest, which was 39.7% higher than that of the control group.

## Effect of pH on lactic acid production in electro-fermentation system

The lactic acid production of the two groups with pH adjusted to 7 at a certain interval was significantly higher than that of the control group with pH not adjusted. The lactic acid concentration in the F-24h group continued to increase during the whole fermentation cycle, the lactic acid yield and maximum lactic acid production rate were significantly higher than those in the control group, and the ORP value of the system was also lower than that in the control group during the whole fermentation cycle. In order to further improve the yield of lactic acid, the adjustment time interval of pH value was shortened to 12h. The maximum lactic acid concentration in F-12h group reached 33.9g/L, which was 208% higher than that in the control group, and the maximum lactic acid production rate reached  $0.435g/(L\cdot h)$ , which was 1.85 times that of the control group. Moreover, ORP had decreased to -248mV at 48h and basically reached the fermentation end point at 96h.



Figure 3 Lactic acid fermentation under different pH regulation frequencies. (A) : F-24h; (B) : F-12h; (C) : NC



Figure 4 Lactic acid fermentation at different pH values

The lactic acid production of all pH regulated groups was significantly higher than that of the control group with unregulated pH value, and the lactic acid concentration increased rapidly within 96h before fermentation, and the maximum concentration appeared at 120h. Among them, the maximum lactic acid concentration of pH7 group was the highest, which was 33.9g/L, 3 times that of NC group, while the maximum lactic acid productivity of pH8 group was the highest within 72h. It is 0.456 g/ (L·h). When the pH is adjusted to 8, more alkali is needed, so in this study, the pH is adjusted to 7 every 12h is the most appropriate condition.

## Effects of pH regulation on microbial community changes during electro-fermentation

In order to clarify the microbial composition of the initial materials before fermentation (INI group) at different pH and the five groups after fermentation 168h in the electro-fermentation system, the microbial community structure after fermentation was analyzed.



Figure 5 Analysis of microbial community structure in electro-fermentation system at different pH. (A): phylum level; (B): genus level

At the phylum level, Firmicutes accounted for the largest proportion of microorganisms in the initial substrate before fermentation (76.7%), followed by Cyanobacteria (18.8%) (see INI column). If no voltage was applied, the proportion of Firmicutes increased to 93.1% after fermentation, and Cyanobacteria almost disappeared (see BLK column). When the pH of the system is low (NC group and pH5 group), the relative abundance of Firmicutes is significantly increased (both over 99.9%). When pH was high (groups pH7 and pH8), the abundance of Firmicutes did not change significantly (62.5% and 77.4%), because the abundance of Actinobacteriota in these two groups was significantly increased (36.8% and 22.6%).

At the genus level, Weissella accounted for the largest proportion (66.1%) in the initial substrate before fermentation, and was a common lactobacillus in food waste. In the BLK group without voltage, Lactobacillus was the dominant strain after fermentation (71.3%), Weissella decreased rapidly, while the proportion of Streptococcus increased (12.2%). The relative abundance of Lactobacillus exceeded 99% when the pH of the system was low (NC group and pH5 group) after 1.0V voltage was applied. When pH is 7, Lactobacillus (44.6%), Streptococcus (5.4%), Enterococcus (5.4%) and Lysinibacillus (5.2%) are the top four Firmicutes. When pH is 8, the abundance of Lactobacillus and Bifidobacterium is lower than that of pH7, while that of Streptococcus and Enterococcus is relatively higher, indicating that these two bacteria are more adapted to the alkaline environment. It can be found that on the basis of adjusting pH, the abundance of Bifidobacterium can be significantly increased after voltage is applied, indicating that this bacterium is sensitive to electrical stimulation.



Figure 6 Correlation analysis between environmental factors and microbial communities. (A) : redundancy

analysis diagram; (B) : Correlation heat map The community composition of NC and pH5 groups is similar, while the microbial community structure of pH7 and pH8 groups is similar. All of them were significantly different from INI group, indicating that the microbial community structure would change significantly after pН adjustment in electro-fermentation. The two environmental factors, pH and ORP, had the greatest influence on the microbial community, and there was a negative correlation between the two environmental factors. For ORP, the community distribution of the starting substrate had the greatest relative influence, while the community distribution of the pH7 group was most affected by pH. The correlation and significance of different species with environmental factors. For the top 10 bacteria with abundance, pH was strongly correlated with the abundance of Lactobacillus, Bifidobacterium, Enterococcus and Actinomyces, among which there was a significant correlation with the abundance of Actinomyces, and the analysis results were statistically significant. ORP is significantly correlated with the abundance of Weissella and Bifidobacterium, and is significantly correlated with the abundance of Weissella.

#### Main metabolic pathways of lactic acid production

The glycolytic pathway, Embden-Meyerhof-Parnas (EMP) pathway, is the main metabolic pathway of lactic acid production in lactic acid bacteria cells. In the glycolysis pathway, the hydrolyzed glucose is first converted into pyruvate through multiple steps, and then regenerated into lactic acid.



Figure 7 Expression levels of major genes in

glycolytic metabolic pathways and enzyme synthesis Compared with the original substrate, the abundance of all enzymes except fructose diphosphate aldolase was upregulated in the system, among which the relative abundance of lactate dehydrogenase was upregulated by 86%. The voltage greatly promotes the fermentation process. For different pH of electro-fermentation, it can be found that when the pH of the system is low (NC, pH5 group), the abundance of metabolism-related enzymes is higher, and when the pH of the second system is high (pH7, pH8 group), the abundance of metabolism-related enzymes is low, which is inconsistent with the previous experimental results. The reason may be that the pH regulation in this experiment is intermittent, so the pH of the system will continue to fluctuate, and the optimal catalytic pH of major enzymes may not be the same as the optimal pH for the growth and reproduction of lactic acid bacteria. As a result, when the pH of the system is low, the life metabolism of lactic acid bacteria is more active, the abundance of enzymes is larger, but the activity of enzymes is low and the catalytic effect is weak. Resulting in lower lactic acid production. When the pH of the system is high, when the pH is in the suitable pH range of the enzyme, the main enzyme can quickly catalyze glucose to lactate. In addition, the catalysis of other enzymes in the system may also affect the production of lactic acid. Therefore, further pH control experiments need to be carried out in order to clarify the situation of probing enzymes in metabolic processes.

#### CONCLUSION

It is feasible to use food waste as a single substrate and apply electrical stimulation to produce lactic acid in open fermentation. In the fermentation process, relatively low voltage has better effect. Adjusting the pH of the system with appropriate frequency can significantly improve the concentration and production rate of acid production. The study found that electro-fermentation promoted the dissolution and hydrolysis of macromolecules, enriched the acid-producing microorganisms, and improved the metabolic process of lactic acid production. The results provide a feasible and effective method for high-efficiency lactic acid production from food waste.

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### Research on the Secondary Photocatalytic Treatment of Effluent from Landfill Leachate Based on Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis

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#### ABSTRACT

In order to enhance the photocatalytic performance and improve the removal of COD and  $UV_{254}$  in leachate, the Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system was constructed, and the concept of secondary photocatalytic treatment was proposed to deeply process the leachate effluent. The stability of Ag3PO4/BiVO4 was also examined.Based on the theory of visible light-assisted photocatalytic activation of PMS, the Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system was constructed to treat leachate effluent. Single-factor experiments were conducted to select the optimal reaction conditions, including PMS concentration, Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> dosage, and reaction pH. The optimal reaction conditions were determined to be 0.5 g Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> + 2.0 g/L PMS in an initial solution with a pH of 11. Under these conditions, the COD was reduced from 242 mg/L to 138 mg/L, UV<sub>254</sub> was reduced from 0.454 to 0.187, and the removal rate was 58.8%. In order to meet the requirements of effluent discharge standards, with COD reduced to 100 mg/L or less, the concept of secondary photocatalysis was proposed. The Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis+P25/UV system used in the secondary photocatalysis process effectively avoided the rapid deactivation of the photocatalyst due to strong adsorption, and achieved the degradation capacity. After the secondary photocatalysis, the COD can be discharged in accordance with the standards, and the humic substances in the leachate are effectively degraded, with a removal rate of 69.5%.In the stability experiment of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> in the Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system for leachate degradation, after four cycles of experiments, the removal rate of COD by Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> remained good, with removal rates of 28%, 28%, 27%, and 24% in four cycles. This proves that Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> has good stability and resistance to photo-corrosion during leachate degradation. The XRD and SEM characterization of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> after use shows that the surface is covered with small molecular substances such as siloxane oxides, which cover the active sites and affect the adsorption of photo-generated charges on the active sites, affect the number of active groups generated, and reduce the photocatalytic activity.

KEYWORDS: Landfill leachate; Photocatalysis; Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis

#### INTRODUCTION

Traditional sanitary landfill technology faces problems such as long stabilization time, complex composition of leachate, and land resource occupation. Therefore, the trend of research is to accelerate the stabilization of waste piles and the degradation of leachate through bioreactor landfill technology[1]. Bioreactor landfill technology uses controlled leachate re-injection to provide suitable oxygen and moisture to the microorganisms in the landfill to enhance the growth and metabolism of microorganisms and maintain a good population structure, so that they produce a series of hydrolases, oxidases, etc. to promote the biodegradation and transformation of organic matter[2]. This accelerates the biodegradation speed of organic waste, reduces the pollution load of leachate, and accelerates the stabilization of bioreactor landfills[3].

Qiu Zhongping et al. [4] found that the COD in the bioreactor after leachate re-injection was reduced from 33,500 mg/L to 3,000 mg/L, with good removal effect. The research group found that the bioreactor landfill technology of leachate treatment and re-injection using mineralized waste can

accelerate the decomposition speed of waste[5]. However, the long-term research shows that the bioreactor landfill system has poor stabilization effect on waste after about one and a half years of operation. According to the decay law of pollution indicators in leachate and the model prediction before the experiment, the COD in the leachate discharged from the fresh waste bioreactor reached 100 mg/L in the fastest case, which required 38 weeks. After running for 78 weeks, the COD concentration of the leachate discharged from the fresh waste was 217.5 mg/L, and it has been around 200 mg/L for a longer period of time.

The BOD<sub>5</sub>/COD value of leachate in the bioreactor landfill operation later is basically less than 0.1, indicating that the leachate at this time is mainly composed of difficult-to-biodegrade organic matter, which is also the reason why the later effect of leachate degradation is poor. Liu Shan et al. [6] By GC-MS, 134 kinds of organic substances, including carboxylic acids, alkenyl hydrocarbons, alcohols and phenols, esters, and ethers, were detected in the leachate after landfilling. These substances, which constitute the difficult biodegradable organic matter, have become the bottleneck in the removal of COD in the bioreactor landfill system [7]. Therefore, developing a technology that can effectively transform and degrade the difficult biodegradable organic matter in leachate at ambient temperature and pressure has become a research trend in the field of leachate treatment.

#### **MAYERIALS AND METHODS**

#### Materials

Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system and P25/UV system (P25 is commercial TiO<sub>2</sub>) were used to compare the effect. Screening suitable secondary photocatalytic systems. The Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system was set as 200mL leachate after primary reaction, 0.5 g Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>, 2.0 g/L PMS, and pH was not adjusted. The P25/UV system was set as 200 mL of leachate after the primary reaction, 0.3g P25, and the pH was not adjusted.

#### **RESULTS AND DISCUSSION**

The removal effect of COD and UV254 in the leachate tail water treated by the combination of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis+P25/UV is shown in Figure 1 (a) and Figure 1 (b). The initial COD of leachate is 194 mg/L, and the COD decreases to 100 mg/L after 30 minutes of dark reaction. After another 60 minutes of photocatalysis, the COD changed to 104 mg/L, and then entered the second-order photocatalysis process. After 30 minutes of dark reaction, the COD decreased to 110 mg/L. The COD values were 96 mg/L, 104 mg/L, and 90 mg/L at every 60 min interval. The values of UV<sub>254</sub> at each time node were 0.38, 0.167, 0.162, 0.156, 0.12, 0.119 and 0.116, respectively. As can be seen from the change trend of COD in FIG. 1 (a), COD decreased obviously in the dark reaction stage of the first-level photocatalysis process, and then the COD concentration increased slightly within 60 min of photocatalysis. In the dark reaction stage of P25, the COD concentration also increased slightly. The increase in this stage can be attributed to the experimental error after the solid-liquid separation, because trace substances in the filter paper after the solid-liquid separation stage may enter the leachate, causing an increase in the COD concentration value. During the 180-min photocatalytic process of P25, the COD concentration showed a dynamic decreasing trend, which was the same as the stage of dynamic COD removal by Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis in Chapter IV. The main reason was related to the complex composition of leachate. A single simulated pollutant has a single component and a single degradation product, so its degradation process can present a stable removal effect. However, the complexity of the composition of leachate makes it face the diversity of degradation processes, as well as the polymerization behavior of degradation products, so that it is in a dynamic removal state. For example, when Zhang Nan et al. [8] used ferrous iron to activate sodium persulfate to treat COD in groundwater contaminated by leachate, the COD also showed a state of dynamic fluctuation. Finally, the COD value of the leachate after secondary photocatalysis was reduced to 90 mg/L, which was less than the discharge standard of the leachate treatment stipulated in the "Domestic Waste Landfill Pollution Control Standard (GB16889-2008)", which is that the COD of the leachate treatment reaches 100 mg/L. Therefore, the leachate in this study can be discharged according to the standard.

In FIG. 1 (b), the removal state of UV<sub>254</sub> shows a different state from COD, and the content of UV<sub>254</sub> shows a continuous decrease during the process of primary and secondary photocatalysis. The adsorption of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> played an important role in the dark reaction stage of first-order photocatalysis, and the degradation of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> was also observed in the photocatalytic stage. In second-order photocatalysis, the decrease of UV<sub>254</sub> was evident during the first 60 min of photocatalysis. The results showed that P25/UV as the secondary photocatalyst also had an obvious effect on the removal of humus. In conclusion, in order to degrade the leachate tail water deeply and avoid the inactivation of catalyst caused by the rapid adsorption of inactive substances, the Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis+P25/UV system used has a significant effect on the removal of leachate and UV<sub>254</sub>. After the treatment, the COD could be discharged to the standard, and the humus in the leachate was effectively degraded, with a removal rate of 69.5%.



Fig. 1 Removing effect of COD and UV<sub>254</sub> in Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis+P25UV combination Stability of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> in Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis system

In order to evaluate the cycling stability of  $Ag_3PO_4/BiVO_4/PMS/vis+$  in visible-light catalytic degradation of tailing water of leachate, cycling experiments were carried out. As PMS is a water-soluble substance, its solubility can reach 250 g/L, so according to the dosage of PMS in this study, PMS will continue to dissolve in water and cannot be separated, and PMS after use cannot be obtained. Considering that PMS is a consumable oxidizer, it is necessary to add new PMS in the next cycle experiment together with the combination of  $Ag_3PO_4/BiVO_4$  after circulation to degrade the leachate again.

Experimental conditions: 200 mL leachate tail water, 0.5 g Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>, 2.0 g/L PMS, pH adjusted to 11. Dark reaction for 30 min and light reaction for 60 min. After the light reaction, the photocatalyst was separated from solid and liquid, rinsed repeatedly with ultra-pure water and anhydrous ethanol, and then the photocatalyst was placed in the oven and dried at 120 °C for 8 h, then ground and reused. As shown in Figure 2, the removal rate of COD by Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> decreased slightly in four cycles of experiments, and the removal rates were 28%, 28%, 27% and 24%, respectively. After four cycles, the removal rate decreased by 3%, indicating that Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> has good stability and photocorrosion resistance during the degradation of leachate. The slight decrease in the degradation rate is due to the continuous cycle of the photocatalyst, the surface of the photocatalyst is continuously covered by small molecule organic matter such as silane oxide, which covers the active site, affects the adhesion of photogenerated charge at the active site, affects the number of active groups generated, and reduces the photocatalytic activity. In general, Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> has relatively good stability and photocorrosion resistance.



#### Fig. 2 Recycling effect of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS degradation leachate



Fig. 3 XRD comparison before and after Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> photocatalysis

Figure 3 is the XRD comparison of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> before and after photocatalysis. The characterization results show that the crystal structure of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> does not change significantly before and after photocatalysis. It was found that the peaks of the photocatalyst were slightly offset after use, which may be due to the fact that Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> was covered with some small molecule organic matter after four times of photocatalysis, which slightly affected the state of the wave crest.FIG. 4 shows the SEM image of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> after photocatalysis. It can be seen from the figure that part of Ag<sub>3</sub>PO<sub>4</sub> loaded on the surface of BiVO<sub>4</sub> after photocatalysis is photocorroded, causing certain damage to the structure of heterojunction. It was obviously observed that some small molecule organic matter in leachate was adsorbed in the material. These small molecules of organic matter are not completely degraded in the reaction process, and the remaining cyclosilicon oxide and other difficult to degrade organic matter. Small molecule organic matter covers the active site on the surface of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>, resulting in the inhibition of the formation of active free radicals. Due to the above two reasons, the photocatalytic effect of COD decreases slightly during the fourth cyclic degradation process.



Figure 4 SEM image of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> photocatalysis

#### CONCLUSIONS

In the initial solution with pH 11, COD and UV<sub>254</sub> decreased from 242 mg/L to 138 mg/L and from 0.454 to 0.187, and the removal rate reached 58.8%. The Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub>/PMS/vis+P25/UV system effectively avoids the rapid deactivation of the photocatalyst caused by strong adsorption in the process of secondary photocatalysis, and gives full play to the degradation ability. After secondary photocatalysis, COD can be discharged up to the standard, and the humus substances in the leachate can be effectively degraded, with a removal rate of 69.5%. Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> has good stability and resistance to photocorrosion during the degradation of leachate. Through XRD and SEM characterization of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> after use, it is proved that the surface of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> is covered with some small molecular substances such as silane oxides, etc., which covers the active site, affects the adhesion of photogenerated charge at the active site, affects the number of active groups, and reduces the photocatalytic activity.

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# MULTIVARIATE STABILIZATION LAW OF THE MICRO-UNIT BIOREACTOR LANDFILL LABORATORY RESEARCH

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#### ABSTRACT

In view of the problems faced by the current sanitary landfill technology in China, such as long stabilization time, difficult pollution control and occupation of a large amount of land, the micro-unit bioreactor landfill technology with batch mulching of humus soil and anaerobic-aerobic multiple stabilization is proposed to break through the bottleneck of the development of existing sanitary landfill technology. Based on this, a simulated micro-unit/conventional bioreactor landfill device was designed in the experiment to conduct a comparative study of anaerobic-aerobic multi-stabilization. The experimental results show that, compared with conventional bioreactors, micro-unit bioreactors exhibit obvious advantages in terms of leachate quality, waste biological stability, and landfill gas composition. The lag phase of anaerobic gas production was shortened to 40 days. The treatment efficiency of the micro-unit reactor is 1.13a-1, which is 12.4 times that of the conventional reactor. This indicates that, compared to traditional anaerobic bioreactors, the micro-unit bioreactor offers higher utilization efficiency and greater economic applicability for landfill space.

#### **0 INTRODUCTION**

Sanitary landfill technology is one of the main treatment methods of domestic waste in China because of its strong economic applicability and relative environmental friendliness [1], but its problems such as long stabilization period [2], air pollution from landfill opening operations [3], and occupation of a large amount of land <sup>[4]</sup> have made sanitary landfill technology face the challenge of being continuously marginalized. Bioreactor landfill is a landfill technology that strengthens microbial processes through purposeful control means to accelerate the transformation and stabilization of easily degradable and moderately degraded organic components in garbage<sup>[5]</sup>, and Professor Pohland F G. <sup>[6]</sup> of the United States took the lead in proposing bioreactor landfill technology in the 70s of the last

century, and Chinese scholars have also carried out related research since the 90s<sup>[7]</sup>. The bioreactor landfill accelerates the stabilization process of domestic waste through leachate recharge<sup>[8]</sup> and aeration<sup>[9]</sup>, reduces the concentration of leachate discharge and treatment costs, and increases the production of landfill gas.

In the early stage, the research group explored the water-gas conductivity of simulated micro-element and conventional bioreactors under different ballast conditions, and simultaneously carried out comparative experiments on anaerobic stabilization efficiency, and understood the anaerobic stabilization law of micro-element bioreactor landfill through the change characteristics of gas-liquid-solid indexes. The results show three that the micro-element bioreactor has obvious advantages in improving the gas-water conduction performance, and the anaerobic stabilization efficiency and gas production efficiency of the simulated micro-element bioreactor landfill are higher than that of the traditional bioreactor under the ballast conditions of 0.1 and 0.2 MPa. By further designing the scale-up micro/conventional bioreactor in the laboratory, the multivariate stabilization law and the spatiotemporal comprehensive utilization efficiency of the two reactors were compared and analyzed.

#### **1 EXPERIMENT**

#### 1.1 Experiment materials and equipment

In the experiment, the prepared domestic waste was prepared with reference to the common components and proportions of domestic waste in the Nanjing transfer station <sup>[10]</sup>, the kitchen waste was collected from the swill bucket in the canteen of the Environmental Science and Technology City, and the other components were obtained from the waste recycling station and crushed to a particle size of less than 100mm, and the proportion and moisture content of each component of the manually prepared domestic waste are shown in Table 1. The humus was taken from the trommel sieve (trommel aperture 60 mm) mined from the Lixin Domestic Waste Sanitary Landfill, which was paved in the shade of the laboratory and dried naturally for three days, and then the sieve was taken through a  $10 \times 10$  mm grid sieve as the coating material of the microelement reactor. The physical and chemical properties of artificially prepared domestic garbage and humus are shown in Table 2. Crushed stone is a material for the preparation of concrete for construction sites, with a particle size of 10-15mm.

| Table1 Components | s, proportion a | nd moisture | content |
|-------------------|-----------------|-------------|---------|
| of                | fabricated MS   | SW          |         |

| Component  | waight/kg | Dereente ge/0/ | water     |  |
|------------|-----------|----------------|-----------|--|
| Component  | weight/kg | reiceinage/70  | content/% |  |
| Food waste | 77        | 70             | 76.8      |  |
| plastic    | 10        | 11             | —         |  |
| paper      | 8.8       | 8              | 9         |  |
| glass      | 4.4       | 4              | 5         |  |
| Textiles   | 3.3       | 3              | 8.4       |  |
| sawdust    | 3.3       | 3              |           |  |
| metal      | 2.2       | 2              |           |  |
| total      | 110       | 100            | 55.4      |  |

| Table2 Physical and chemical properties of       |
|--|
| artificially prepared domestic garbage and humus |

| Water<br>content<br>(%) | properti<br>es | $AT_4$<br>(mgO <sub>2</sub> /g<br>DW) | BDM<br>(%) | VS(%) |
|-------------------------|----------------|---------------------------------------|------------|-------|
| 55.38                   | waste          | 287.58                                | 87.5       | 80    |
| 3.81                    | humus          | 4.54                                  | /          | /     |

Design and manufacture of plexiglass columnar microelement reactor (hereinafter referred to as "MR") and conventional reactor (hereinafter referred to as "CR") experimental device (Fig. 1), the total height of the device is 2280mm,.



### Fig.1 Schematic diagram(left) and physical picture(right) of micro-unit bioreactor

The MR filling height is 2080 mm, the bottom and top are filled with gravel layers with thicknesses of 280 mm and 200 mm respectively, and four micro-element landfill units are arranged in the middle, each unit is 350mm high garbage layer and 50mm high humus layer from bottom to top, and the garbage layer is 20mm annular humus layer, 130mm annular garbage layer, 20mm annular humus layer, 20mm annular gravel layer and 20mm perforated PVC pipe from outside to inside. From the outside to the inside, the humus layer consists of a 170mm annular humus layer, a 20mm annular gravel layer and a 20mm perforated PVC pipe (Fig. 2 (right)).

The CR filling height is 1400mm, the bottom and top are filled with 300mm and 200mm gravel layers respectively, the middle part is 900mm high garbage layer, and the garbage layer is 170mm annular garbage layer, 20mm annular gravel layer and 20mm perforated PVC pipe from the outside to the inside.



Fig.2 Top view of waste layer (left) and humus layer (right) of micro-unit reactor

#### 1.2 Design of experiment

In the micro/conventional reactor stabilization comparison experiment, the leachate at the bottom of the device was emptied every other day and fully recharged into the reactor through a peristaltic pump, with a reinjection rate of about 100mL/min and a reinjection time of about 1 h. The leachate was retained before daily reperfusion and the pH, COD, NH3-N and TN indexes were sampled and measured. After the reactor started gas production, the daily gas production was recorded, the landfill gas was collected every other day to determine the methane volume fraction

#### **1.3 Analytical Methods**

The pH, COD, NH3-N, and TN of the leachate water samples were determined by reference to the standard method [11], and the VFAs of the water samples were distilled and determined by gas chromatography external standard method. The daily gas production is read by a wet gas flow meter, and the methane volume fraction is determined by gas chromatography external standard method.

#### 1.4 Data analysis

The theoretical gas production of indoor garbage is based on the IPCC model, and the calculation formula is shown in equation (1).

$$L_0 = 1867 \times \sum \left[ W_t \times (1 - d_t) \times DOC_t \times m_t \right]$$
(1)

where:  $L_0$  is the gas production potential of garbage per unit mass, in terms of wet basis, L/kg; 1867 is the conversion coefficient between organic carbon and the volume of landfill gas under standard conditions. DOC is the total degradable organic carbon content, calculated on wet basis, kg/kg; Wi is the wet weight content of a degradable component, %; di is the moisture content of a degradable component, calculated on a wet basis, %; DOCi is the organic carbon content of a degradable component, calculated on a dry basis, %; mi is the biodegradability rate, calculated on a dry basis, %.

The biochemical reaction of microorganisms plays a leading role after the degradable organic matter in domestic waste enters the rapid degradation stage, and the change of leachate COD can be approximated by the exponential decay model, which is calculated in equation (2).

$$C = C_0 \exp\left(-kt\right) \tag{2}$$

where: is the leachate COD,  $mg \cdot L^{-1}$ ; is the initial concentration of leachate COD when it begins to degrade,  $mg \cdot L^{-1}$ ; k is the degradation rate constant of organic matter, d<sup>-1</sup>; t is the running time, d

For the methane production stage of anaerobic fermentation in the landfill process, the modified Gompertz equation <sup>[16]</sup> (3) can be used to fit the cumulative methane yield. For the anaerobic stabilization phase after the hysteresis period, the first- order kinetic equation (3) can be used for fitting.

$$P = p_m \times \exp\{-\exp\{-\exp\left[\frac{p_m \cdot e}{p_0}(\lambda - t_1) + 1\}\right]$$
(3)

$$P = P_M \times (1 - e^{-\kappa t_2}) \tag{4}$$

where: P is the cumulative methane yield at time t, L/kg wet basis; Pm is the final cumulative methane yield, L/kg wet base; Rm was the maximum methane production rate, L·kg-1 wet base  $d^{-1}$ ; is the gas-producing hysteresis phase, d; is the running time of the anaerobic stabilization process, d; is the anaerobic stabilization rate constant,  $d^{-1}$ ; is the operating time after deducting the lag period time, d. In order to quantitatively characterize the waste treatment capacity of the landfill, the volume of waste that can be processed per unit volume per unit time is defined as the  $\gamma$  of the landfill's treatment efficiency, and the calculation formula is shown in equation (5). The ratio of the reactor processing efficiency is defined as the spatiotemporal conversion rate, which is calculated in equation (6).

$$\gamma = \frac{V_{MSW}}{V_L \cdot T} \tag{5}$$

$$\delta = \frac{\gamma_M}{\gamma_C} \tag{6}$$

where: is the landfill treatment efficiency, d-1; is the initial volume of garbage, m3; is the volume of the landfill, m<sup>3</sup>; is the stabilization period, d; for the spatio-temporal conversion rate; for micro-element landfill treatment efficiency; It is the efficiency of conventional landfill disposal.

#### **3 RESULT & DISCUSSION**

#### 3.1 Leachate water quality

Fig. 3 shows the change trend of the pH of the leachate of the micro/conventional reactor, and the pH value of the leachate in the anaerobic stabilization stage is similar, showing the characteristics of first decreasing and then increasing, but the pH value of the microelement reactor decreases less and rises faster. The pH of the microelement reactor was stable at 8.5-8.8 before the end of anaerobic, and the pH fluctuated from 8.0-9.0 during operation after switching to the aerobic stabilization stage, while the pH of the conventional reactor was close to 6.5 when the operation was terminated and did not enter the aerobic stage.

The initial stage of anaerobic stabilization of perishable organic compounds in domestic waste is

the process of hydrolysis and acidification, and the acidic inhibition of organic acid products is the main reason for the initial hysteresis period of anaerobic stabilization. The micro-element reactor adopts humus coating structure to provide a weak alkaline environment with neutralization and buffer organic acids, which alleviates the problem of acid inhibition in the early stage of anaerobic stabilization, and makes the micro-element reactor transition to the stable methane production stage quickly. Due to the constraints of the conventional reactor, the plant is still in the anaerobic hysteresis period before the plant is stopped, and the pH value of the leachate is always lower than 6.5, which is in the state of acid inhibition.



Fig.3 pH variation of leachate in micro-unit/conventional reactor

Fig. 4 is the change of COD in the leachate of the microelement/conventional reactor, the COD change law of the leachate is about the same at the beginning of operation, and all of them show the characteristics of rapid increase, but the peak concentration of the microelement reactor is lower (ML is 51419.86mg/L, CL is 66399.68mg/L) and decreases rapidly after reaching the peak, the COD concentration is maintained at about 5000mg/L before the end of the anaerobic stage, and the COD value of the leachate does not change significantly at the beginning of the aerobic stage, with the enhancement of oxygen supply, The COD of leachate gradually increased to 8000mg/L. The conventional reactor is always in the anaerobic hysteresis period during operation, and the COD value of the leachate remains high after the reaction.

At the beginning of operation, microorganisms use the organic matter in the solid waste to produce a large amount of organic acids through hydrolysis and acidification, so the COD of the leachate of the two reactors rises rapidly. The weak alkaline environment of the humus cladding layer in the microelement reactor can alleviate the acid inhibition problem in the early stage of anaerobic stability, make the leachate pH rise rapidly and reach the suitable growth pH range of methanogens, and the continuous use of volatile fatty acids makes the leachate COD value decrease rapidly, and in the aerobic stage, part of the refractory organic matter is decomposed into intermediate pollutants, resulting in the increase of leachate COD value .



Fig.4 COD variation of leachate in micro-unit/conventional reactor

Fig. 5 shows the change diagram of VFAs of microelement/conventional reactor, which rises
rapidly and gradually stabilizes at the beginning of operation, and then decreases rapidly and stabilizes at 1500mg/L until the end of the anaerobic stabilization stage of microelement. The conventional reactor gradually stabilized after a rapid ramp-up at the beginning of operation, and did not show a downward trend until the end of operation.

At the beginning of the operation of micro-element and conventional reactors, the organic matter in the solid-phase waste was converted into soluble organic acids through microbial hydrolysis and acidification, which led to a rapid increase in the concentration of VFAs in both reactors. The concentration of VFAs in the micro-element reactor reached the peak faster and its peak concentration was only 1/4 of that of the conventional reactor, which was mainly due to the adsorption and retention effect of the humus coating layer of the micro-element reactor on organic matter, and the weak alkaline environment of the humus itself would neutralize some organic acid molecules to form acid ions, and at the same time inhibit the activity of hydrolyzed acidifying bacteria. During the operation of the conventional reactor, the pH of the leachate is always less than 6.5, and the activity of hydrolytic acidification bacteria is strong, and the microorganisms produce a large number of organic acids through hydrolysis and acidification, resulting in the inability of methanogens to survive. Therefore, the leachate VFAs cannot be degraded and maintained at high concentration levels.



Fig.5 VFAs variation of leachate in micro-unit/conventional reactor

Figure 6 shows the NH<sub>3</sub><sup>-</sup>N variation diagram of the microelement/conventional reactor. The NH<sub>3</sub><sup>-</sup>N concentration in the micro-element reactor showed a trend of rapid increase-slow decrease-stability, while the NH<sub>3</sub><sup>-</sup>N concentration in the conventional reactor tended to be stable after a rapid increase, and the peak and stable values of ammonia nitrogen in the micro-element reactor were lower than those in the conventional reactor.

In the initial stage of anaerobic stabilization, macromolecular organic compounds such as proteins in micro/conventional reactors are decomposed into small nitrogen-containing organic compounds through hydrolysis and then converted into NH<sub>3</sub><sup>-</sup>N through the deamination process, so the NH<sub>3</sub><sup>-</sup>N concentration in both reactors increases rapidly. After entering the aerobic stage, a large amount of water is carried away by ventilation, resulting in an increase in the concentration of NH<sub>3</sub><sup>-</sup>N in the leachate, and it is expected that the NH<sub>3</sub><sup>-</sup>N concentration of further aerobic ventilation will decrease.



Fig.6 NH<sub>3</sub>-N variation of leachate in micro-unit/conventional reactor

Figure 7 shows the TN variation of microelement/conventional reactor. The total nitrogen concentration of micro-element/conventional reactors showed a trend of rapid increase-slow decrease-stable trend, but the peak TN and stable values of micro-element reactors were lower than those of conventional reactors, and the attenuation amount and attenuation time were higher than those of conventional reactors.

The concentration of NH3-N in the leachate of micro/conventional reactor accounted for more than 70% of the TN concentration, which was mainly due to the fact that ammonia nitrogen could not be converted into nitrate nitrogen by nitrification under anaerobic conditions, so the total nitrogen in the leachate mainly existed in the form of inorganic ammonia nitrogen. The coating structure and buffering effect of humus soil are conducive to the growth of microorganisms and the removal of ammonia nitrogen, so the TN of the microelement reactor has a higher attenuation amount and attenuation time.



Fig.7 TN variation of leachate in micro-unit/conventional reactor

#### 3.2 Gas indicator

#### 3.2.1 Theoretical gas production

According to the PICC model, the theoretical gas production potential L0 of the microelement reactor is 157.42 L·kg-1 wet basis. In the "Specification", the IPCC model calculates that the final gas production potential of China's domestic waste L0 is 121.7 L·kg-1 wet basis, and the Land GEM-China model calculates that L0 is 112 L·kg-1 wet basis, and the theoretical gas production potential of domestic waste in the microelement reactor is high, which may be due to the artificial preparation of domestic waste in this experiment, and the content of kitchen waste accounts for about 70% of the total domestic waste, while the content of kitchen waste in the "Specification" only accounts for 43.6%. As a result, the theoretical gas production potential L0 is higher than the calculated value of the IPCC model and the GEM-China model in the Specification.

# **3.2.2 Daily gas production and cumulative gas production**

Figure 8 is the daily gas production diagram of the microelement reactor. In the anaerobic

stabilization stage of the micro-element reactor, the daily gas production showed a trend of rapid increase-stabilization-slow decline, while the conventional reactor was still in the anaerobic hysteresis period before the end of the reaction and did not produce gas.

The weak alkaline environment covered by humus in the micro-element reactor neutralizes and buffers a large number of organic acids produced by hydrolysis and acidification in the early stage of anaerobic stabilization, so that the reactor quickly enters the stage of stable methane production, and in the later stage of anaerobic stabilization, most of the easily degradable organic matter has been converted into humus by methanogens, and ammonia nitrogen cannot be degraded under anaerobic conditions, resulting in an increase in pH value and inhibiting the activity of methanogens.



Fig.8 Variation law of daily gas production of micro-unit reactor

Fig. 9 is the fitting diagram of the modified Gompertz equation for the cumulative gas production rate of the microelement reactor. The trend of cumulative gas production during the anaerobic stabilization process of the microelement reactor was fitted by the Gompertz equation, and the final cumulative gas yield Pm was 127.64 L·kg-1 wet basis under the experimental conditions in the laboratory. When the actual cumulative gas production rate of the micro-element reactor reaches 90% of the final cumulative gas production rate, the gas production rate will continue to decrease, and the anaerobic system will enter a period of decline. Therefore, the anaerobic stabilization of the microelement reactor was switched to the aerobic stabilization stage after the 173rd day.



Fig.9 Variation trend of cumulative gas production in micro-unit reactor and fitting curve of modified

#### Gompertz equation

Laboratory experiments generally have higher k values due to their small volume and supplemented by leachate circulation and pH adjustment. The stabilization rate constant of domestic waste in landfill is generally obtained by on-site gas extraction experiments, and due to the different biodegradation stages of garbage, the K value obtained by on-site gas extraction experiments is widely distributed, generally 0.02-0.2y<sup>-1</sup>.

The parameters related to the gas production of micro/conventional reactors are summarized in Table 2.

Table 2 Summary of relevant parameters of

| reacto<br>r | Theoretic<br>al gas<br>productio<br>n<br>potentialL<br>0/(L*kg <sup>-1</sup><br>wet) | Lag<br>perio<br>dλ | $\begin{array}{l} Final \\ cumulative \\ gas \ P_m / \\ (\ L^*kg^{-1}Vw \\ et \ ) \end{array}$ | Stabiliz<br>ation<br>rate<br>constan<br>t k/a <sup>-1</sup> |
|-------------|--|--------------------|--|---|
| ML          | 157.42   | 40                 | 127.64   | 2.65  |
| CL          | 157.42   | /                  | /  | /   |

micro-unit/conventional reactor gas production

## **3.2.3** Methane volume fraction and cumulative methane production

Figure 10 shows the trend of methane volume fraction of microelement reactor gas. The change trend of methane volume fraction in the landfill gas of microelement reactor is about the same as that of daily production, and both gas show the characteristics of rapid increase, tend to be stable, and slowly decrease. Before the end of the anaerobic phase, the methane volume fraction is less than 40%, which does not belong to the high-efficiency methane production stage.



Fig.10 Change trend of methane concentration in micro-unit reactor

Fig. 11 is the fitting diagram of the modified Gompertz equation for the cumulative methane production of the microelement reactor. The final cumulative methane yield Pm(CH<sub>4</sub>) was 69.4 L·kg<sup>-1</sup> wet base, and the maximum methane yield Rm(CH<sub>4</sub>) was 0.717 L· (kg·d)<sup>-1</sup> wet base, the methanogenic hysteresis period was 44d, and the R<sup>2</sup> was 0.999. After the cumulative methane yield P0 (CH<sub>4</sub>) reached 90% of the final cumulative methane yield  $P_m$  (CH<sub>4</sub>), the methane production rate continued to decrease, and the anaerobic stability entered the decline phase, so the microelement reactor was switched from the anaerobic stabilization aerobic stage to the stabilization stage.

The parameters related to methane production in reactors are summarized in Table 3.

Table3 Summary of parameters related to methane production of micro-nuit/conventional

| Teactor |                            |                                |  |  |
|---------|----------------------------|--------------------------------|--|--|
|         | Theoretical                |                                |  |  |
| naaatan | methane                    | Final methane yield            |  |  |
| reactor | yieldL <sub>0(CH4)</sub> / | $P_{m(CH4)}\!/~(L*kg^{-1}wet)$ |  |  |
|         | $(L^{kg^{-1}wet})$         |                                |  |  |
| ML      | 78.71                      | 69.4                           |  |  |
| CL      | 78.71                      | /                              |  |  |



Fig.3.5 Variation trend of cumulative methane production in micro-unit reactor and fitting curve of modified Gompertz equation

#### 3.3 Spatiotemporal conversion rate

Assuming that the time required for the micro/conventional reactor to reach 90% degradation rate is used as the anaerobic stabilization time, the relevant parameters of the spatiotemporal conversion rate of the micro/conventional reactor are summarized in Table 4.

# Table 4 Parameters related to space-time conversion rate of micro-nit/conventional reactor

| rec<br>tor | Plo<br>t<br>rati<br>o | Anae<br>robic<br>stabil<br>izatio<br>n<br>time/<br>d | Lag<br>period<br>of<br>anaerob<br>ic<br>aerobic<br>switchi<br>ng/d | Aer<br>obic<br>stabi<br>lizat<br>ion<br>time<br>/d | Proce<br>ssing<br>effici<br>ency/<br>a <sup>-1</sup> | Spatio<br>tempo<br>ral<br>conver<br>sion<br>rate |
|------------|-----------------------|--|--|--|--|--|
| М          | 0.6                   | 168  | 15   | 11   | 1.13   |  |
| L<br>CL    | 5<br>1                | 4015   | /  | /  | 0.091  | 12.4   |
|            | -                     |  | •  | ·  |  |  |

#### **4 CONCLUSION**

1) Compared with conventional reactors, the degradation rate of leachate COD and VFAs is faster due to the buffering effect and better gas-water conduction performance of humus, and the ammonia nitrogen and total nitrogen are maintained at a higher concentration level due to the inability to degrade under anaerobic conditions. The buffering effect of the humus cladding layer on acid inhibition in the microelement reactor can shorten the gas production lag period to 40 days, and the actual methane

production during the operation period can reach more than 90% of the maximum methane production.

2) The spatiotemporal conversion efficiency of the anaerobic stage of the micro-element reactor was 12.4, indicating that the micro-element bioreactor had a higher utilization efficiency of landfill space.

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## DUAL NATURE OF NONCATALYTIC HYDROTHERMAL DECHLORINATION KINETICS OF PVCS

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#### ABSTRACT

Noncatalytic hydrothermal dechlorination kinetics of polyvinyl chloride (PVC) have traditionally been regarded as a single-step process, which fails to capture the dynamic nature of the mechanism. This study reveals that dechlorination is a dual process, encompassing a slow chemical-reaction-controlled stage followed by a rapid mass-transfer-controlled stage, observed in PVC with degrees of polymerization (DP) of 480, 1050, and 3000. In the initial stage, nucleophilic substitution plays a significant role in the reaction mechanism, while the latter stage is primarily driven by an elimination mechanism. The onset of mass transfer limitations is marked by a discontinuity in the first-order reaction plots within a dechlorination degree range of 50 %-56 %. The activation energy (EA) for PVC480, PVC1050, and PVC3000 is 213.5, 219.8, and 225.0 kJ/mol, respectively, during the chemical-reaction-controlled stage, and 244.9, 203.3, respectively, and 202.2 kJ/mol, in the mass-transfer-controlled stage. When particle aggregation occurs, thermal dehydrochlorination parallels hydrothermal dechlorination, as both processes exhibit two-stage kinetics, are prone to mass-transfer limitations at the latter stages, and the reaction rate is influenced by the propagation of the zipper mechanism along the chain length in nonisomerizing PVCs. This study provides a detailed analysis of hydrothermal dechlorination kinetics, contributing to a more comprehensive understanding of PVC hydrothermal degradation chemistry.

**KEYWORDS:** PVC; Hydrothermal dechlorination; Kinetics; Autocatalysis

#### INTRODUCTION

Polyvinyl chloride (PVC), the third most produced plastic in Japan, is primarily disposed of through incineration [1]. This method, however, raises significant environmental concerns due to the emission of chlorinated compounds, dioxins, and corrosive hydrogen chloride gas. As such, shifting toward the chemical recycling of PVC is critical for achieving a circular economy and mitigating these adverse effects. Central to this process is hydrothermal dechlorination, which aims to replace chlorine atoms in PVC with hydroxyl groups, producing environmentally benign and easily liquefiable intermediates [2]. Despite its potential, the realization of efficient hydrothermal dechlorination has been hindered by a limited understanding of the reaction kinetics and underlying chemistry, with existing research often resulting in only partially hydroxylated products.

The mechanism of hydro/solvothermal dechlorination operates dynamically, with competitive nucleophilic substitution and elimination playing distinct roles depending on factors such as temperature, additives, solvent compatibility, and the degree of dechlorination. Previous reports [3], [4] suggest that hydrothermal dechlorination is a single-staged process, typically described by a single kinetic parameter throughout, or at least assumed to remain constant during the main process. Conventionally, dechlorination reaction parameters are determined by fixing the reaction time interval and varying the temperature. While not inherently incorrect, this methodological simplification introduces inconsistencies by potentially conflating reaction rate constants from different stages of the process. Such conflation poses challenges in accurately determining kinetic parameters and can lead to misunderstandings of hydrothermal dechlorination. This approach results in truncated dechlorination profiles, offering insufficient data to detect discontinuities in first-order plots, which mark the transition of reaction regimes. This limitation underscores the need for a more comprehensive kinetic analysis to accurately capture the intricacies of the noncatalytic hydrothermal dechlorination process.

By providing a detailed analysis of noncatalytic hydrothermal dechlorination kinetics, this paper clarifies the dynamic nature of dechlorination, addressing inconsistencies in previous research. Through this work, we contribute to a more comprehensive understanding of PVC's hydrothermal degradation chemistry, paving the way for more effective reaction control in recycling strategies.

#### MAYERIALS AND METHODS Materials

Three pure and additive-free PVC (purity  $\ge 99.9$  %) with particle sizes of less than 100  $\mu$  m and degrees of polymerization (DP) of 480, 1050, and 3000 were selected for these experiments. These samples are referred to as PVC480, PVC1050, and PVC3000, respectively.

# Hydrothermal dechlorination experiments and hydrochar characterization

In each experiment, a sample of PVC  $(0.1 \pm 0.005 \text{ g}, \text{containing 56.7 \% chlorine by weight)}$  was combined with 10 ml of distilled water and placed into a 28 cm3 polytetrafluoroethylene (PTFE) reactor. The sealed reactor was then positioned in a preheated oven set to the desired reaction temperature. Throughout the reaction, the reactors were agitated at a speed of 33 rpm, and the process was terminated by quenching in a cold-water bath after a predetermined reaction time. Following the reaction, the solid byproducts were separated by filtration, dried, and securely stored for subsequent analysis. All hydrothermal dechlorination experiments were conducted in duplicate to ensure repeatability and minimize errors.

Hydrochar was qualitatively and semi-quantitatively characterized using Fourier transform infrared spectroscopy (FT-IR; model 4600 from JASCO, Japan), X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific ESCALAB 250XI+).

#### **RESULTS AND DISCUSSION**

## Effect of depolymerization degree on hydrothermal dechlorination

Fig. 1 (a) reveals that below a dechlorination extent of 40 %, the rate follows the trend: PVC480 > PVC1050 >PVC3000. This is due to the delayed onset of thermal degradation temperature for thermally stable PVCs. While dechlorination initiation is delayed for PVC3000, it accelerates faster than other PVC polymers, particularly when dechlorination exceeds 54 %. This surge in reaction rate indicates a deviation from a linear relationship and marks the onset of a different dominant mechanism. For PVC480, dechlorination increases steadily, while PVC1050 shows the slowest rate. To investigate the phenomena underpinning these observations, first-order kinetics were determined, and the plots are presented in Fig. 1 (b). Hydrothermal dechlorination occurs in two distinct regimes: a slow step where water plays an active role, and a rapid step where the involvement of water is passive. The discontinuity in the first-order plots signifies the

transition from one reaction regime to another.



**Fig. 1.** (a) Effect of time on hydrothermal dechlorination of PVCs at 230 °C and (b) corresponding first-order reaction plots.

The precise point of transition is marked by a star in the figure and can be determined by solving the simultaneous equations representing these plots. As dechlorination progresses, residual organic chlorine is encased in a progressively growing, partially hydroxylated polyene structure [1], gradually rendering the interior impenetrable to hydroxyl nucleophilic attack. This shift indicates a transition from a chemical

reaction-controlled to a mass transfer-controlled mechanism.

The reaction rates for both the initial and later stages follow the order: PVC3000 > PVC480 > PVC1050. This pattern mirrors that observed in the first stage of thermal dehydrochlorination, suggesting that the reaction rate is predominantly influenced by the progression of the zipper mechanism. Additionally, the ratio of the reaction rate in the mass-transfer-controlled stage to the chemical-reaction-controlled stage is approximately 2.4 for PVC480 and PVC3000, while for PVC1050, it is 2.8. The differences in these observations are attributed to the overall mechanism and structure of the nascent hydrochars formed during the process.

#### FTIR analysis of hydrochars

The primary identifier for organic chlorine in pristine PVC is depicted by the sharp peak at 615 cm<sup>-1</sup>, attributed to the stretching vibrations of C-Cl, as shown in Fig. 2 (a). Secondary peak identifiers include bands at 1250 cm<sup>-1</sup> and 1300 cm<sup>-1</sup>, which are attributed to -C-H stretching in -CHCl groups. In addition, there is a peak at 2960 cm<sup>-1</sup> corresponding to the stretching vibrations of -C-H adjacent to the primary functional group. Chemical transformations of the PVC surface can be monitored qualitatively by tracking changes in the spectrum. After hydrothermal dechlorination, the primary and secondary peaks progressively decrease with reaction time, while new prominent peaks at 1700 cm<sup>-1</sup> (C=C) and 3000 cm<sup>-1</sup> (C=C-H) emerge and slightly increase in intensity. The emergence of these peaks indicates dechlorination via the elimination reaction, which occurs through the zipper mechanism, wherein a conjugated polyene structure is formed by the release of hydrogen chloride. The propagation of polyene growth is limited by the presence of the hydroxyl functional group at 3500 cm-1, which can be introduced into the polymer chain through nucleophilic substitution. Therefore, the dechlorination process occurs via competitive nucleophilic and substitution reactions. The ensuing section will quantify the contributions of these mechanisms to the dechlorination process.

XPS analysis was conducted various on semi-dechlorinated PVC samples, each with а dechlorination degree of 65.1  $\% \pm 1.2 \%$  (Fig. 2 (b-d)). Although the dechlorination degree is consistent across samples, the relative intensities of different functional groups vary significantly (Table 1). For PVC3000, the relative intensity of C=C at 23 % is slightly greater than for PVC480 at 19 %, which can be attributed to the enhanced propagation of the polyene structure associated with high DP PVC (Table 1). This observation is supported by the higher maximum DTG observed in PVC3000 compared to other polymers. The intensities for C=C are about twice that of C–OH for PVC480 and PVC3000 hydrochars, suggesting a predominance of the elimination mechanism over substitution.





**Fig. 2.** (a) Typical FTIR spectra for hydrothermally treated PVC and (b-d) deconvoluted XPS spectra for semi dechlorinated PVC at a dechlorination degree of 65.1%.

**Table 1.** XPS deconvoluted peak areas for semi-dechlorinated PVC (DE= $65.1 \% \pm 1.2 \%$ ).

| Senn deenno | initiated 1 v | C(DL 0.0.1) | 1/0 - 1.2/0 | ·)·  |
|-------------|---------------|-------------|-------------|------|
| Functional  | Binding       | PVC         | PVC         | PVC  |
| group       | energy        | 480         | 1050        | 3000 |
|             | eV            | %           | %           | %    |
| C=C         | 287.5         | 19.4        | 15.9        | 23.0 |
| C-C/C-H     | 289.5         | 47.4        | 34.0        | 38.5 |
| C-Cl        | 290.4         | 23.4        | 34.5        | 28.3 |
| C-OH        | 291.5         | 9.8         | 15.6        | 10.2 |

In contrast, the results for PVC1050 show equal intensities for C=C and C-OH, while the concentration of C-Cl is unusually high. A plausible explanation for this is molecular isomerization, which has formed a chlorine-rich surface, facilitating accessibility to hydroxyl nucleophiles and thus enabling unencumbered competitive elimination and substitution reactions. This could explain the suppressed reaction rate observed for PVC1050 in the chemical-reaction-controlled stage. As a result, a relatively hydroxyl-rich polyene structure is formed. Such a polyene structure, laden with oxygen heteroatoms, results in a less compact and relatively porous shell which could enhance PVC-hydrochar wettability and facilitate the diffusion of hydroxyl ions into the particle interior. Similarly, this type of shell could decrease diffusion resistance to hydrogen chloride gas or inorganic chlorine from the semi-dechlorinated hydrochar. This might explain why the reaction rate of PVC1050 in the mass-transfer-controlled stage is 2.8 times that of the chemical-reaction-controlled stage, compared to approximately 2.4 times for the other PVC polymers.

#### CONCLUSIONS

Contrary to existing literature that portrays hydrothermal dechlorination as a single-step process, our findings indicate that it is a two-stage process. Initially, there is a slow chemical-reaction-controlled stage characterized by significant contributions from nucleophilic substitution and elimination reactions, followed by a rapid mass-transfer-controlled stage where the elimination mechanism predominates. The reaction rate of the latter stage is generally at least twice that of the former. The transition between stages is marked by a break in linearity in the first-order plots, typically occurring at a dechlorination degree of 50 %-56 % within the studied temperature range. This study provides a detailed analysis of hydrothermal dechlorination kinetics, enhancing our understanding of the dynamic nature of the dechlorination process and contributing to a more comprehensive understanding of the hydrothermal degradation chemistry of PVC.

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# FIELD SIMULATION OF ALKALI MODIFIED COAL FLY ASH FOR SOIL AMENDMENT

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#### ABSTRACT

A large number of coal fly ash (CFA) harmful byproducts produced by coal-fired power plants are not utilized efficiently and must be treated urgently. Arid and semi-arid areas such as Inner Mongolia, China have dry climate and low soil quality and poor water retention, which will affect the yield and diversity of crops. In this paper, CFA was calcinated with different proportions of alkali (KOH) and applied to soils with different initial moisture contents to improve soil water retention capacity and inhibit soil cracking. The results showed that alkali (KOH) and calcination treatment of CFA noticeably enhanced the evaporation mitigation capacity (EMC) of the soil. Compared with OS, the addition of KOH modified CFA in soil could induce the improvement of EMC to 19.43% (40% initial moisture, KC21), 21.96% (10% initial moisture, KC11), 23.02% (20% initial moisture, KC21), 23.35% (10% initial moisture, KC21), and 52.03% (10% initial moisture, KC31). Field-scale simulation proposes that KOH-modified CFA amendment could retain 14% of irrigation water mass in soil by evaporation inhibition.

**Keywords:** Coal fly ash, Soil amendment; Evaporation mitigation capacity; Field simulation

#### **INTRODUCTION**

Human activities like pollution, exploiting natural land for farming, and overgrazing are main reason for desertification, soil degradation and drought. Desertification directly has negative effect on 250 million people in the developing world, which might extend with climate change and growth of population.

In drought land, soil moisture is insufficient for crop in specific growth stage to maintain normal physiological process, e.g. respiration and homeostasis of cells, tissues, organs and plants, leading to reduced production and food insecurity<sup>1</sup>. Therefore, in order to keep crop yield in current and future serve environment, release plant stress of insufficient soil water is urgent. Adding soil amendment to retain water in soil is an effective measurement to reduce irrigation frequency<sup>2</sup>. Coal fly ash contains a series of plant essential elements, this unique property makes it to be used as soil amendment. Previous studies have shown that application of CFA facilitated crop growth by increasing nutrients supply, such as K, Na, Fe, Mg, Ca, Si and Se<sup>3,4</sup>. Due to the special physical property like fine particle and low density and inner porosity, application of CFA under suited ratio into soil can improve soil physiochemical properties, thus promote crop growth and yields<sup>5</sup>. The low sulfur content and the presence of magnesium carbonate and calcium carbonate hydroxide, resulting in the alkaline CFA. CFA could be added in to acidic soil to increase soil pH<sup>6</sup>. Moreover, CFA is mainly composed of silica and alumina, making it potentially to be used as low-cost adsorbents for pollutant reduction and water amelioration7. Previous work reported that raw CFA had the positive impact on soil water retention capacity<sup>7</sup>, but this effect didn't lead to significant improvement. Therefore, new methods should be investigated to treat CFA that can increase water retention capacity in soil drastically.

Therefore, alkaline modified CFA was prepared in this study aiming at improving the soil EMC notably. To address the research gaps, the objectives of this study include: (1) study the effect of CFA and modified CFA on soil EMC, (2) simulate the water holding capacity of soil with CFA and modified CFA after agricultural irrigation in 1 acre field. The results of this study may provide a distinctive alternative way to utilize CFA in soil amendment.

#### MATERIALS AND METHODS

Before treatment, CFA was dried in an oven at 105  $^{\circ}$ C for 24 h. Then, KOH and CFA were mixed at different ratios, and deionized water was also added into the mixture. After 10 min standing time, mixtures in crucibles were calcinated in a muffle furnace at 500  $^{\circ}$ C for 1 h, and the calcinated residue was collected for further analysis.

Akatama soil was used in this study, which was crushed and sieved smaller than 75  $\mu$ m. Before EMC test, CFA, KOH modified CFA and soil were dried in an oven at 105 °C for 24 h to eliminate moisture inference. Then soil was mixed with raw CFA (R-CFA), calcinated-CFA (C-CFA), calcinated KOH-modified CFA (KOH:CFA=1:1 (KC11), KOH:CFA=2:1 (KC21), and KOH:CFA=3:1 (KC31)) respectively. EMC was tested at 3 initial moistures (10%, 20% and 40%) under 6 conditions (Only Soil (OS), Raw CFA (R-CFA), C-CFA, KC11, KC21 and KC31) with 1 hour interval.

#### **RESULTS AND DISCUSSION**



Figure 1 The reduced amount of evaporated water in additives amended soil compared to

#### in OS.

CFA and modified CFA could be applied in soil as soil conditioners due to their properties, inhibiting the development of cracks on the soil surface and alleviating the evaporation of water in the soil. Combined with the temperature changes in Lamawan town, Qingshuihe County, Hohhot City, Inner Mongolia in summer, the amount of water evaporation after adding additives in 1 acre field was analyzed (compared with OS), and the reduction in evaporation within 24 hours after irrigation was simulated (Fig. 1). According to the temperature change curve, the temperature was higher during the period of 09:00 to 21:00, thus the data of the reduced amount of evaporated water at 40 °C was used for simulation during this period, and the data at room temperature was used for the other lower temperature time periods. Irrigation time was set at 9 am in summer. As shown in Fig. 1, the addition of RCFA or CCFA slightly reduced evaporated water. However, adding KC11, KC21, and KC31 drastically reduced evaporated water. The decrease of water evaporation by additives (CCFA, KC11, KC21 and KC31) was a parabola-like behavior, increased first, reached the highest value in the 6th hour of irrigation, and then decreased. The effect of reducing evaporation could last up to the 13 hours after irrigation. Among them, KC21 performed the best, with a maximum reduction of 38.623 kg per acre (14.027% of total irrigation water mass 275.397 kg) compared with OS. However, after 13 hours of irrigation, the addition of CFA and modified CFA lost the advantage of reducing evaporation, and even increased evaporated water compared with OS. In fact, after rainfall or irrigation, plants will adsorb soil water by roots due to soil moisture levels and their specific requirements. Water adsorption process is relatively short, and plant's water uptake reaches its peak within a few hours. In addition, at that time, the temperature was relatively low, and plants no longer photosynthesize, and the intensity of transpiration was weakened. Therefore, after 13 hours of irrigation, the impact of changes in ability to reduce evaporation ignoreable.

#### CONCLUSIONS

The modified CFA increased the EMC more significantly than raw CFA. Field scale simulation of soil with CFA additives could inhibit evaporation to keep irrigation water in soil.

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## **RESEARCH PROGRESS ON RESOURCE UTILIZATION OF BY-PRODUCTS FROM CORNN STARCH PROCESSING**

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ABSTRACT: Corn is widely used in food processing, livestock feeding, fertilizer and bio-medicine industries. Corn deep processing industry is one of the main application fields of corn. Corn starch, corn edible oil and so on are the products of corn deep processing. In the process of corn starch processing, a series of by-products, such as corn husks and corn pulp, will be produced. These by-products have the problem of high fiber content and low availability. With the increase of people's demand for corn starch, the production of corn starch gradually increases, and the by-products produced in the processing process also increase, which means that a large number of by-products of corn starch processing need to be treated and utilized, which has great research potential.

At present, some by-products are used in some fields. As a low-value by-product, corn husks contain a lot of cellulose, hemicellulose and a small amount of lignin, protein and other substances, which are gradually used as feed for livestock farming, but there are still some substances that have not been fully treated and are fully utilized, and the amount of affected areas is limited. In addition, corn pulp is rich in protein, contains a certain amount of sugar, nitrite and other substances, and has not been well treated and reused.

The characteristics, treatment methods and

comprehensive utilization of by-products of corn starch processing were described in this paper. The aim is to explore the treatment technology of corn starch processing by-products and improve the utilization value of corn processing by-products.

#### **INTRODUCTION**

Corn is one of the world's highest sown area and total output of crops, because of its short growth cycle, high survival rate is considered to be an important grain, has a high economic value and nutritional value, plays an important role in human society. Corn is not only used as a food source and animal feed, but also processed into corn products and chemical products after biological, physical and chemical treatment. Corn deep processing production is one of the main fields of corn utilization. Corn starch is one of the important products of corn deep processing<sup>[1]</sup>. At present, the mainstream of the corn starch industry is mostly the wet production of corn starch. During the processing of corn starch, some by-products with low added value and high fiber content are produced. With the gradual increase of people's demand for corn starch, the output of corn starch production is also increasing, and the by-products produced in the production process are also increasing. Improper disposal and treatment will cause

environmental pollution problems and make it impossible to realize the rational use of such waste. According to the composition and structural characteristics of these by-products (corn husks), certain pretreatment is required for reuse. The present research shows that the by-products of corn starch processing after biological, physical and chemical treatment can be used to describe the characteristics of corn starch processing by-products in different fields, and explore the technical methods and application prospects of corn deep processing by-products reuse.

### 1 CORN STARCH PROCESSING TECHNOLOGY

At present, the corn starch processing technology used in the starch processing industry is mainly divided into dry method (Fig.1) and wet method (Fig.2). The differences between the two methods are mainly reflected in raw material treatment, reaction conditions, production process, product characteristics and environmental impact.



Fig.1 Dry process flow of corn starch production



Fig.2 Wet process flow of corn starch production

When selecting the processing method, it should be comprehensively considered according to the specific needs, production costs, environmental protection requirements and other factors. The dry process has low cost, short process and does not use water, but the product may have some structural damage; Although the wet process is costly and water intensive, it can produce high-purity starch products and effectively separate the by-products for further use. At present, wet processing of corn starch is the main advantage in industrial production.

#### 2 TYPES OF CORN STARCH PROCESSING BY-PRODUCTS

The by-products in the wet processing of corn starch have wide application value. Through reasonable development and utilization, these by-products can not only bring additional economic benefits for enterprises, but also realize the comprehensive utilization of resources and the sustainable development of the environment<sup>[2-4]</sup>.

#### 2.1 Corn steep liquor

The liquid after concentration treatment is corn pulp. Corn pulp was rich in soluble protein (45.69%), total sugar (0.2650 g/L) sulfite (0.10%), dissolved phosphorus (10443  $\mu$ g/g) and other components, and was acidic (pH=3.8). Corn pulp is a good nutrient source for microbial fermentation, which can be used to cultivate various microorganisms, and can also be used as raw material for feed yeast to improve the nutritional value of feed.

#### 2.2 Corn husk

In the corn starch production process, after the germ has been effectively separated, it is further screened by a curved screen. In this step, the main component of the sifted material is corn husks. Corn husk is a nutrient-rich byproduct that contains a lot of cellulose and hemicellulose, as well as small amounts of beneficial components such as protein and lipid.Fig.3 shows the analysis of corn husk components. With its rich nutritional value, corn husks can be widely used as feed, food and other industries.



Fig.3 Analysis of corn husk components

#### 2.3 Corn germ

Corn germ is rich in oil and is an important raw material for producing corn germ oil. Rich in a variety of nutrients, such as vitamin E, protein, phospholipid, etc.can be used as health care products and cooking oil.

#### 2.4 Zein

Corn gluten meal contains a high proportion of protein, can be used as an additive in food, can also be used as a high-protein component of animal feed. In addition, corn protein can be further processed into bioactive substances such as corn peptides.

#### 2.5 Other

In addition to the above-mentioned by-products, there are corn germ meal, corn starch residue and so on.

### 3 PRETREATMENT METHOD CORN HUSK

The by-product of corn starch processing -corn husk, for example, has the following components: cellulose (39.03%) hemicellulose (36.77%) lignin (5.16%) ash (3.5%).

Because corn husk contains a large number of fiber components, in order to improve the full utilization of corn husk and the quality of subsequent products, pretreatment is usually carried out. The common chemistry pretreatment methods for such biological resources include low temperature medium acid (LTMA), high temperature dilute acid (HTDA), alkali pretreatment (AP) and sulfite pretreatment (SP).

#### 3.1 Low temperature Medium Acid (LTMA)

At lower temperatures and moderate acidity, the polymer in biomass (such as cellulose, hemicellulose and lignin) will degrade, producing a large number of low molecular weight compounds (such as methanol, acetic acid, etc.). These low molecular weight compounds have higher reactivity, which is conducive to subsequent conversion and utilization. Low temperature treatment helps to reduce energy consumption and equipment investment costs, while avoiding excessive loss of active ingredients in biomass at high temperatures; Avoiding moderate acidity

conditions can accelerate the degradation process of biomass while avoiding serious corrosion of equipment.

#### 3.2 High temperature dilute acid (HTDA)

Under the conditions of high temperature (usually higher than 100°C) and dilute acid (such as dilute sulfuric acid), polymer such as cellulose and hemicellulose in biomass will be hydrolyzed to produce low molecular weight monosaccharides such as glucose and xylose. These simple sugars can be used as substrates for microbial fermentation and further converted into biofuels such as ethanol or chemicals. High temperature helps to accelerate the hydrolysis reaction and improve the conversion of biomass. Dilute acids can reduce the activation energy of the reaction, promote the hydrolysis of biomass, and also prevent excessive degradation of biomass during pretreatment, thus maintaining a high sugar recovery rate.

#### 3.3 Alkali Pretreatment (AP)

The principle of alkali pretreatment of biomass is mainly to use alkaline solution to destroy and degrade lignin, hemicellulose and other components of biomass, so that it is easier to be converted by microorganisms or other chemical methods. Under alkaline conditions, the bonding bonds between lignin and hemicellulose are broken, making these components easier to separate and extract. Alkali pretreatment is usually carried out under milder conditions than other pretreatment methods. In addition, alkali treatment will destroy the fiber structure in the biomass, making it fluffy, increasing the surface area, and improving the accessibility of the substrate to enzymes.

#### 3.4 Sulfite pretreatment (SP)

In the pretreatment process, sulfites can penetrate into the interior of the biomass, react with functional groups such as phenolic hydroxyl groups in the lignin, destroy the structure of the lignin, and make it easier to be used by enzymatic hydrolysis or fermentation microorganisms. The acidity of sulfites can also promote the hydrolysis of hemicellulose to produce useful components such as oligosaccharides and monosaccharides. Compared with harsh conditions such as high temperature and pressure, sulfite pretreatment is usually carried out under milder conditions, which is conducive to reducing energy consumption and costs.

There have researched that compared the above four pretreatment methods of biomass, and showed that the effect of sulfite pretreatment of fibrous biomass was better than the other three methods, and found that the waste liquid of sulfite treatment contained high value byproduct xylooligosaccharide<sup>[5]</sup>.

In the follow-up study, in order to avoid the influence of other cations, sulfite solution was selected to pretreat corn husks, and then the next step was carried out.

### 4 COMPREHENSIVE APPLICATION OF CORN HUSK 4.1 Feedstuff

Compared with fish meal and bean cake commonly used in feed industry, corn husk as feed material has the advantages of cheap and easy to obtain, high feeding value and safe composition. Gu Keke et al. explored the value of corn starch processing by-products in feeding and the technology of improving quality and efficiency<sup>[6]</sup>. Li Shiyao et al. evaluated the effect of fermented corn processing by-products and raising livestock<sup>[7]</sup>.

#### **4.2 Food industry**

Corn husks have a high fiber content, which can be further processed to produce dietary fiber and improve human intestinal digestive health. Devin J Rose et al. explored the extraction of useful ingredients from corn husks for the production of food ingredients or additives and food chemicals<sup>[8]</sup>. Wei Xuyao et al. optimized the extraction process of dietary fiber from corn husk by using complex enzyme modification<sup>[9]</sup>. **4.3 Culture strain**  Corn husks contain a lot of polysaccharides, which are dissolved into monosaccharides after pretreatment, and its hydrolysate can be used as a nutrient source for fungus culture. Therefore, corn husks can also be used as raw materials for yeast feed. Liu Yuchun et al. studied the cultivation of Aspergillus Niger and Trichomorhynchus with corn husk fiber as carbon source<sup>[1]</sup>.

#### 4.4 Other

(1) Corn husks were used as substrate, microbial fermentation was added, and the fermentation products were collected and reused.

(2) Cellulose and other organic nutrients in corn husks, after fermentation or compost, can be made into organic fertilizer.

We are also exploring the use of sugar in the dissolved solution of corn husks after acidification as carbon source and organic protein in corn pulp as nitrogen source to cultivate microorganisms and produce fertilizer.

#### **5 OUTLOOK**

The resource utilization of corn processing by-products will become an important direction of future research

#### 5.1 Feed industry

Corn processing by-products have broad application prospects in the field of feed. By optimizing the formulation and processing process, these by-products can be converted into high-quality, low-cost feed raw materials. This can not only reduce the cost of feed production, but also improve the nutritional value of feed and promote the development of animal husbandry.

#### 5.2 Food industry

With the rapid development of the food industry, the demand for natural, healthy and nutritious food raw materials is increasing. Some components of corn processing by-products have unique nutritional value and functional properties, such as flavin and zein active peptide. In the future, these ingredients will be more used in the food industry to develop more food with health functions.

#### 5.3 Environmental protection field

Corn processing by-products also have potential application value in the field of environmental protection. For example, corn starch wastewater could be used to produce biofertilizers or biofuels; Renewable energy such as biogas is produced by anaerobic fermentation of waste such as corn germ meal. These applications can not only reduce environmental pollution, but also realize the recycling of resources.

#### ACKNOWLEGEMENT

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## MOLECULAR TRANSFORMATION OF DISSOLVED ORGANIC

## MATTER DURING PHOTOCATALYTIC DEGRADATION OF HUMIC

### ACID BY SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> HETEROJUNCTION

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Abstract: By exploiting Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O absorbs carbon dioxide in the air to produce Na<sub>2</sub>CO<sub>3</sub> and Sn(OH)<sub>4</sub>, a novel Z-type heterojunction photocatalyst SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was created using Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O (supplying both Sn source and CO<sub>3</sub><sup>2-</sup>) as precursors. The preparation of the photocatalyst was verified by comprehensive characterization. Under the condition of simulated visible light irradiation for 120 min, the removal of UV<sub>254</sub> from 20 mg/L humic acid (HA) by SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> reached 81.72%, and the removal of color number (CN) reached 82.41%. The results of fluorescence excitation emission matrix (EEM) and parallel factor analysis (PARAFAC) showed that C1-C3 could be degraded by photocatalysis. Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to investigate the transformation characteristics of dissolved organic matter (DOM) from the molecular structure. It was discovered that photocatalysis mainly breaks down most CHO and CHON compounds, significantly reducing the variety of organic substances (from 7240 to 4018). The removal of organic matter primarily occurs through reactions involving carboxylic acids, oxygen addition, and dealkylation. The study provides a straightforward and workable approach for the preparation of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> photocatalyst with good recyclability and reusability, and provides a reference for understanding the DOM changes in HA during photocatalysis.

#### INTRODUCTION

Water pollution caused by the discharge of refractory organic matter in the water environment has become an urgent concern and has attracted extensive global attention [1]. Humic acid (HA) is a typical refractory organic substance, which is widely present in natural water bodies and various types of wastewaters, such as domestic sewage, livestock and poultry wastewater, landfill leachate, and papermaking wastewater [2-5]. The macromolecular backbone of HA consists of aromatic and aliphatic residues and contains a large number of substituents, such as phenols, ketenes, amino acids, and carboxyl groups [6]. Removal of HA is necessary before chlorination of drinking water, as reactions between HA compounds and disinfectants can cause side effects that may lead to the risk of cancer and reproductive problems, and trigger the growth of algae

and microorganisms in water distribution pipes [7]. To date, various techniques have been developed for the removal of HA, encompassing advanced oxidation processes (AOPs), biodegradation, filtration, and adsorption [8-11]. Despite the widespread utilization of adsorption in water treatment for HA removal, this approach still encounters challenges associated with the costly regeneration process of the adsorbent [7]. The treatment of organic matter using AOPs has garnered significant attention due to its inherent advantages of rapid oxidation kinetics and absence of secondary pollution [12]. Among these methods, the photocatalytic approach is widely recognized as an effective means for degrading HA, owing to its costeffectiveness, simplicity in operation, and high efficiency [13, 14].

Photocatalytic technology utilizes semiconductor

photocatalysts to oxidize or reduce pollutants by utilizing reactive species, such as electrons e<sup>-</sup> and h<sup>+</sup>, generated under light irradiation [15]. When the photocatalyst is exposed to light with energy greater than its band gap (Eg), an e- in the valence band (VB) transitions to the conduction band (CB), creating  $h^+$ . The resulting electron-hole pairs can facilitate the formation of active substances like 'O2' and 'OH during their separation and transfer processes [16]. These reactive species then undergo redox reactions with organic matter, leading to the decomposition of large organic compounds into smaller molecules for effective removal [17]. In recent years, metal oxide semiconductors have emerged as promising photocatalysts for the degradation of environmental pollutants due to their abundance, low cost, chemical stability, and excellent photocatalytic activity [18]. Among these semiconductors, SnO<sub>2</sub> stands out not only for its stable physical and chemical properties but also for its wide availability, non-toxic nature, and affordability [19]. As a result of these advantageous characteristics, it has been extensively employed in various applications related to wastewater treatment through photodegradation processes [20]. Nevertheless, one significant drawback associated with SnO<sub>2</sub> lies in its wide band gap that limits its photoactivity solely under UV light exposure conditions [21]. Solar irradiance reaching the Earth's surface predominantly comprises around 45% visible light ( $\lambda = 400-700$  nm) while ultraviolet radiation ( $\lambda < 387$  nm) accounts for less than 5%. Consequently, the solar photocatalytic activity of SnO<sub>2</sub> photocatalyst is constrained [22].

Several strategies have been proposed to enhance the photocatalytic activity of  $SnO_2$ , including doping [23], formation of nanocomposites [24], construction of heterojunctions [25] and photosensitization with dyes [26]. Among the various modification techniques, constructing a heterojunction between two semiconductors is a well-established method to improve the photocatalytic efficiency of semiconductor materials [27, 28]. Pheiroijam Pooja et al. [27] prepared Cu<sub>2</sub>O-SnO<sub>2</sub> p-n heterojunction and showed promising application prospects in the field of efficient degradation of organic wastewater, with about 100% degradation of methylene blue and methyl orange at 30 min and 35 min, respectively. Sifan Chen et al. [29] fabricated a branched SnO<sub>2</sub>@ZnO heterojunction photocatalyst via a facile two-step hydrothermal synthesis method and observed that the degradation efficiency of rhodamine B using the SnO<sub>2</sub>@ZnO heterojunction photocatalyst reached approximately 97% after an illumination time of 80 min, while the photocatalytic efficiencies of ZnO and SnO<sub>2</sub> were around 90% and 55%, respectively. It is believed that the introduction of heterojunctions can promote charge transfer. inhibit the recombination of photogenerated electron-hole pairs, and further improve the photocatalytic activity. Based on the aforementioned analysis, it is reasonable to speculate that the incorporation of heterojunctions can enhance the photocatalytic activity of SnO<sub>2</sub>. Relevant investigations have demonstrated that Z-type heterojunctions actively participate in photocatalytic reactions by exhibiting robust redox capability [30]. Therefore, exploring and developing emerging Z-type heterojunctions holds significant meaning and importance in achieving efficient photocatalytic reactions.

The interchanging energy band structure of SnO<sub>2</sub> and Bi2O2CO3 can effectively construct a Z-type heterojunction, facilitating the separation and migration of photogenerated charge carriers while preserving the original redox ability of SnO2 and Bi2O2CO3 to enhance photocatalytic activity. Currently, many researchers prepare Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> by adding carbonate as a reactant with  $Bi(NO_3)_3 \cdot 5H_2O$ . This work takes advantage of the fact that Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O can absorb carbon dioxide in the air to form Na<sub>2</sub>CO<sub>3</sub> and Sn(OH)<sub>4</sub>, and combines the Na<sub>2</sub>CO<sub>3</sub> produced by Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O with Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O to form Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> Z-type heterojunction photocatalytic materials with different composite ratios were prepared by a one-step hydrothermal method. Comprehensive characterization and evaluation were conducted on the morphology, chemical composition, photoelectric properties, performance, and stability of HA photocatalytic degradation for the SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> materials. To facilitate practical applications, we also investigated the effects of material amount, HA concentration, pH values variations as well as anions on the photocatalytic reaction. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was employed to analyze changes in DOM following photocatalytic degradation of HA at the molecular level. Furthermore, the mechanism underlying the degradation photocatalytic process mediated by SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was also explored. This research provides valuable insights into synthesizing SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> heterojunction photocatalysts through a one-step hydrothermal method without requiring additional carbonates and provides a reference for understanding the changes of organic matter in HA during photocatalytic degradation.

#### MATERIALS AND METHODS

#### Preparation of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>

The preparation of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is shown in Fig. S1, and the detailed operation is as follows: 5 mmol Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O was weighed and dissolved in 30 mL ultrapure water and sonicated for 10 min, followed by the addition of 0.5 mmol CTAB for 10 min to form a homogeneous solution. 5 mmol Bi(NO3)3 · 5H2O was weighed and dissolved in 30 mL ultrapure water and sonicated for 10 min to form homogeneous solution B. Solution A was slowly added to solution B, and after 10 min of sonication, the mixture was moved to a Teflonlined stainless-steel autoclave for thermal processing at a temperature of 200 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature Subsequently, the resulting mixture was harvested via centrifugation and subjected to thorough washing with ultrapure water followed by absolute ethanol. Finally, obtained precipitate were dried at 80 ° C for 8 h. Controlling the molar ratio of Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O and  $Bi(NO_3)_3 \cdot 5H_2O$  to be 0.5, 0.75, 1 and 2 to prepare different ratios of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> samples, named as 0.5 SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, 0.75 SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>,  $2SnO_2/Bi_2O_2CO_3$ , respectively. The preparation of pure SnO<sub>2</sub> and Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> were described in Supporting

Information.

#### Test of photocatalytic degradation of HA

The photocatalytic activity of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was investigated using HA as the target pollutant. Weighed 0.10 g of the prepared catalyst in a 1000 mL beaker, and 200 mL of HA solution (20 mg/L) was slowly poured into the beaker, placed in a dark room and stirred for 30 min to achieve adsorption-desorption equilibrium. The light source (300 W xenon lamp) was turned on, and the light source was 15 cm away from the solution. A certain amount of samples were taken every 15 min, and the supernatant was selected by centrifugation to determine the absorbance. The absorbance was tested at 254 nm using a UV-vis spectrophotometer. C/C<sub>0</sub> was used to represent the removal effect of the catalyst, where C<sub>0</sub> and C are the absorbance of the HA solution at 254 nm before the photoreaction and at a certain time, respectively. The color number (CN) was calculated as CN = $\frac{A^2_{436}+A^2_{525}+A^2_{620}}{A_{436}}$ , where A<sub>436</sub>, A<sub>525</sub> and A<sub>620</sub> represent the  $A_{436} + A_{525} + A_{620}$ absorbance values at 436, 525 and 620 nm wavelength,

#### **RESULTS AND DISCUSSION**

respectively.

#### Characterization of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>

The crystal structure of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> composites in the series was analyzed using XRD. As shown in Fig. 1a, the peak at  $2\theta = 26.61^{\circ}$  corresponds to the (110) and (200) crystal planes of SnO<sub>2</sub>, which is consistent with the standard card for SnO<sub>2</sub> (JCPDS:41-1445) [31]. The diffraction peaks observed at 12.93°, 23.90°, 26.03°, 30.25°, 32.73°, 39.50°, 42.30°, 46.97° and 56.89° can be attributed to the (002), (011), (004), (013), (110), (006), (114), (020) and (123) planes respectively of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> according to its standard card(JCPDS:41-1488) [32]. These results indicate successful preparation of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. FT-IR spectroscopy was used to analyze the composition and functional groups of the prepared samples. As shown in Fig. 1b, the absorption peaks in the 1611 cm<sup>-1</sup> and  $3200 \sim 3600$  cm<sup>-1</sup> regions are attributed to the O-H vibration of the adsorbed water on the sample surface [33]. The absorption peak of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> at 548 cm<sup>-1</sup> comes from the stretching vibration of Bi-O [34], while the two absorption peaks at 850 cm<sup>-1</sup>, 1390 cm<sup>-1</sup> and 1465 cm<sup>-1</sup> come from the bending mode and antisymmetric vibration mode of  $CO_3^{2^-}$  [35], respectively. For pure SnO<sub>2</sub>, the absorption band near 640 cm<sup>-1</sup> corresponds to the Sn-O stretching vibration [36]. The major absorption peaks induced by SnO<sub>2</sub> and Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> can be found in all the SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> composites, further confirming the successful fabrication of the SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> composites.



Fig. 1. XRD (a) and FTIR (b) patterns of the prepared samples

XPS was used to investigate the elemental composition and chemical state on the surface of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> catalyst. High-resolution XPS spectra of Sn, Bi, O, and C were shown in Fig. 2a-d. As shown in Fig. 2a, the binding energies of Sn 3d in SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> are 494.5 eV and 486.1 eV, corresponding to Sn 3d3/2 and Sn 3d5/2, corresponding to  $Sn^{4+}$  [20]. Comparing the Sn 3d peak in pristine SnO<sub>2</sub>, it can be found that the binding energy of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is lower than that of SnO<sub>2</sub>. Compared with the original Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, the corresponding binding energies of Bi 4f7/2 and Bi 4f2/5 in SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> shifted from 159.12 and 164.48 eV to 158.8 and 164.1 eV, respectively, corresponding to Bi<sup>3+</sup> [37]. The O 1s spectrum of the catalyst is shown in Fig. 2c and can be divided into a lattice oxygen of 530.0-530.7 eV and a surface adsorbed oxygen of 532.1-533.2 eV [38]. The C 1 s spectrum of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> shows peaks at 288.6 eV and 284.8 eV corresponding to carbonate and standard carbon references [39]. The slightly lower binding energy of the carbonate peak (287.4 eV) after SnO<sub>2</sub> binding is due to the change in the chemical environment after SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> recombination, where the strong interaction changes the electronic distribution of the C atom [40], which is similar to the findings of Bai et al. [41].



Fig. 2. XPS profiles of SnO<sub>2</sub>, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> photocatalytic materials: (a)Sn 3d, (b) Bi 4f, (c) O 1s, (d) C 1s.

The optical absorption characteristics are considered to be important for improving the photocatalytic efficiency, UV-vis-DRS was used to evaluate the optical absorption properties of the prepared photocatalysts [39]. As shown in Fig. 3, the absorption intensity of the composite catalyst SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> increased compared with SnO2 and Bi2O2CO3, and the light absorption range expanded to visible light. This result is mainly due to the successful synthesis of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> heterojunctions. The Eg of SnO<sub>2</sub>, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is determined by the Tauc formula:  $\alpha hv = A(hvEg)^{n/2}$  [42]. As shown in Fig. 3, the Eg of SnO<sub>2</sub>, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> were 2.93 eV, 2.83 eV and 2.76 eV, respectively. The E<sub>VB</sub> can be calculated using VB-XPS. The EVB of SnO<sub>2</sub>, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> were 2.00 eV, 0.91 eV, and 2.10 eV, respectively (Fig. 3). According to the formula  $E_{CB} = E_{VB} - E_g$ , the conduction band ( $E_{CB}$ ) can be calculated to be about -0.93 eV, -1.92 eV and -0.66 eV, respectively.



Fig. 3. (a)UV-vis diffuse reflectance spectra, (b) Tauc plots and (c)VB-XPS spectra

#### Photocatalytic performance

The photocatalytic degradation efficiency of the obtained catalysts was evaluated under xenon lamp irradiation using simulated HA wastewater as the treatment subject. The dark reaction was carried out for 30 min before photocatalytic degradation to achieve adsorption equilibrium, and all the photocatalytic materials showed relatively low adsorption rates. As shown in Fig. 4a, the UV<sub>254</sub> removal rates of HA by single photocatalyst SnO2 and Bi2O2CO3 were only 15.34% and 18.18%, respectively, and CN removal rates were 12.52% and 28.00%, respectively. The degradation efficiency of HA with different composite ratios of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was significantly improved, because the electron-hole pairs of the composite materials could be better separated. The removal rates of UV<sub>254</sub> on HA by 0.5SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, 0.75SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>,  $SnO_2/Bi_2O_2CO_3$ ,  $2SnO_2/Bi_2O_2CO_3$ were 31.71%, 44.95%, 81.72% and 70.34%, respectively. The removal rates of CN were 37.37%, 45.65%, 82.41% and 75.40%. At the same time, a first-order kinetic curve was fitted (Fig. 4b), and it was found that the fitted curve was close to a linear curve, which proved that the photocatalytic degradation process conformed to pseudo-first-order kinetics [43]. In addition, the degradation rate constant of  $SnO_2/Bi_2O_2CO_3$  (0.0147 min<sup>-1</sup>) was 9.19 times higher than that of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (0.0016 min<sup>-1</sup>), indicating that the SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> composite had a high photocatalytic degradation efficiency.



Fig. 4. Degradation curves of SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> under visible light and (b) pseudo-first-order kinetics. **EEM spectra characterizations of DOM** 

The EEM data from samples during photocatalysis were successfully decomposed into four distinct components using PARAFAC modeling (Fig. 5). The C1 peak was observed at Ex/Em = 250, 450/533 nm, the C2 peak at Ex/Em = 500/590 nm, and the C3 peak at Ex/Em= 250, 315/463 nm, all of which exhibited humic-like fluorescence characteristics [44-46]. The C4 was located at Ex/Em = 250/533 nm and could be associated with a humic-like component or aromatic conjugated macromolecular substances of terrestrial origin [47, 48]. Typically, longer wavelength fluorescence peaks are structural associated with condensation and polymerization of humus [49]. Hur et al. [50] showed that the fluorescence signature at longer emission wavelengths was more pronounced in the EEM of humus fractions with larger sizes. In this case, the humic-like components can be distinguished by their different molecular weights, with an order of C2 > C1 > C3.



Fig. 5. Identified EEM-PARAFAC components of C1,

#### C2, C3 and C4.

# Molecular transformation of DOM after photocatalytic degradation

FT-ICR MS was employed to comprehensively investigate the molecular composition and transformation properties of DOM during the photocatalytic degradation of humic acid wastewater. DOM composition in raw water and humic acid solution after photocatalysis was assessed using Van Krevelen plots (Fig. 6). In the VK plot, different colors indicate identified DOM types, which can be categorized into four groups based on their elemental composition: compounds containing only C, H, and O (CHO), compounds containing S (CHOS), compounds containing N (CHON), and compounds containing both S and N (CHONS). Regions I-VII represent lipids, proteins, carbohydrates, unsaturated hydrocarbons, lignins, tannins, and aromatic structures, respectively [51]. Following photocatalytic treatment, the concentration of HA decreased significantly along with a reduction in total organic matter from 7240 to 4018. Before and after photocatalytic degradation, aromatic structures and lignin constituted the major components of the HA solution accounting for 45.97% and 40.86%of total organic matter before degradation, whereas after degradation accounted for 18.71% and 44.51%, respectively. CHO and CHON compounds were predominant before and after photocatalytic degradation, however, there was an increase in CHOS compounds from 6.52% to 17.65%, while CHONS compounds increased from 3.16% to11.47%.



Fig. 6. Van Krevilen diagram. (a) Raw water (HA, 20

mg/L), (b) After photocatalysis, (c) and (d) bar chart of organic matter quantity.

The differences in molecular composition of CHO, CHON, CHOS and CHONS removed by photocatalysis were compared using Kendrick mass defect (KMD) analysis. According to the definition of KMD, DOM with the same KMD belongs to a series of homologs that differ solely in terms of their molecular weights, exhibiting a molecular weight interval ( $\Delta m$ ) that is an integer multiple of the mass associated with the selected functional group [52]. At equivalent KMD values, the DOM exhibits higher Kendrick nominal mass due to an increased presence of repetitive functional groups [53]. Fig. 7a demonstrates a decrease in Kendrick nominal mass under identical KMD-COO values after photocatalytic degradation, indicating effective degradation of COO groups during photocatalysis. Additionally, Fig. 7b reveals a decreasing trend in KMD-CH<sub>2</sub> value after photocatalytic degradation, suggesting demethylation also as a predominant pathway for refractory organic compounds. To understand the transformation pathway of DOM, mass difference analysis is an effective method to link precursors and products [54, 55]. Fig. 7c provides a statistical breakdown of molecular reactions involving DOM, encompassing oxygen addition reactions (26.27%), dealkylation reaction (24.10%), carboxylic acid reactions (27.94%), amine reactions (4.59%), sulfate reactions (1.37%), and other miscellaneous reactions (15.73%). Furthermore, linkage analysis was conducted on 32 transformation reactions occurring in DOM precursor products (Fig. 7d), revealing reaction of carboxylic acid (-C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>/-C<sub>3</sub>H<sub>2</sub>O<sub>2</sub>), reaction of dealkylation  $(-C_3H_4/-CH_2)$ , and oxygen addition (+O/+3O) as the most common reaction types.



Fig. 7. Kendrick mass defect analysis during photocatalytic process (a–b), number of each reaction type (c), radar plots of links detected in the transformation of HA (d).

#### CONCLUSION

In this work, a novel Z-type heterojunction photocatalyst SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was synthesized by a onestep hydrothermal approach utilizing Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O (which provides both Sn and CO<sub>3</sub><sup>2-</sup> by absorbing  $CO_2$  in the air). During the preparation,  $Bi(NO_3)_3 \cdot 5H_2O$  reacts with the given  $CO_3^{2-}$  to generate Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> without the need for extra carbonate supply. The results showed that after 120 min of simulated visible light irradiation, the removal rate of  $UV_{254}$  of 20 mg/L HA by SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (molar ratio of Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O and Bi(NO<sub>3</sub>) <sub>3</sub> · 5H<sub>2</sub>O is 1) reached 81.72%, and the removal rate of CN reached 82.41%. The SnO<sub>2</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> catalyst exhibited excellent reusability, with sustained UV254 removal rate of 72.52% even after undergoing four cycles. The transformation of DOM during the photocatalytic degradation of HA was investigated at the molecular level using FT-ICR MS, which revealed a significant decrease in CHO and CHON organoids accompanied by an increase in refractory organic compounds, CHOS and CHONS. In the process of photocatalytic degradation, lignin and aromatic structural compounds of DOM are degraded mainly through carboxylic acid reaction, oxygen addition reaction and decalkylation reaction to form a large number of fatty acid-like compounds. This study can provide reference for the photocatalytic degradation of HA by SnO<sub>2</sub>/ Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> heterojunction photocatalyst.

#### ACKNOWLEDGEMENTS

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## **Estimation of Plastic Fishing Gear Marine Leakage from Fishing Vessel Fisheries in Japan**

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#### Abstract

Marine plastics are recognized as an important issue that urgently needs to be resolved. A survey of drifted litter conducted by the Ministry of the Environment at 10 beaches across Japan reported that approximately 70% of the litter that drifted ashore by weight was plastic products, including fishing gear, and that litter from the fishing industry accounted for approximately 30% of the total. Therefore, this study aimed to estimate the national marine discharge of plastic fishing gear used for fishing boats and used at sea and in the sea. Specifically, the amount of plastic fishing gear discharged into the ocean per ton of catch using three survey methods ((1) a survey in which fishermen were asked to record fishing gear discharges during operations, (2) a survey combining fishing gear purchase records of fishermen and a questionnaire on the rate of fishing gear discharges into the ocean, and (3) an interview survey with fishermen) was estimated and multiplied by the national catch by fishing method. Nine fishery types were surveyed: purse seine, set net, trawl net, gill net, scoop net, basket net, longline fishing, squid fishing, and towline fishing. The results showed that an estimated 2,507 tons of plastic fishing gear was estimated to be discharged into the ocean from Japan's fishing vessels in one year. Characteristics of fishing methods that are more likely to result in gear being spilled include fishing methods that use fishing lines and fishing methods in which the gear is independent of fishing vessels and people.

#### **1. INTRODUCTION**

Marine plastics are recognized as a critical environmental issue that demands urgent resolution. According to a survey on coastal debris conducted at ten locations across Japan by the Ministry of the Environment, approximately 70% of beach litter by weight comprises plastic products, including fishing gear, with around 30% originating from the fishing industry. However, there have been limited quantitative studies on the loss volume of plastic fishing gear from fisheries.

This study aims to estimate Japan's national volume of plastic fishing gear leakage into the ocean from fishing vessel fisheries, particularly focusing on plastic fishing gear used on the water surface or in the sea. We conducted an investigation on nine types of fisheries, including purse seine, set net, trawl, gill net, scoop net, pot trap, longline, drifting barrel, and trolling in the Kyushu and Hokkaido regions, estimating the loss volume per unit catch of plastic fishing gear and the loss rate into the ocean.

#### 2. ESTIMATION OF PLASTIC FISHING GEAR LEAKAGE

#### 2-1 Methodologies

To estimate the marine leakage of plastic fishing gear, this study employed three research methods: (1) operational records, (2) purchasing records and survey on loss rates, and (3) interviews with fishermen. We calculated the unit loss by dividing the estimated loss of plastic fishing gear during the survey period by the fishing activity volume. Some fishing gear, such as nets and artificial lures, contain non-plastic materials like lead and aluminum, but this study focuses on plastic fishing gear, which may include non-plastic materials as well.

#### (1) Estimation based on operational records

This survey targeted longline fishing, squid fishing (floating fishing), and trolling. Fishermen were asked to record details in their operation logs over a three-month period if any plastic fishing gear was lost during their activities. The log items included the type and quantity of fishing gear used on that day, the type and quantity of gear lost, among other details, enabling an estimate of the amount of loss as described later. To convert the recorded quantity of lost gear into weight, standard fishing gear actually used in each fishing method was provided, and weights were measured by gear type. The marine plastic fishing gear loss  $D_1$  (kg) during the survey period was estimated using Equation (1), by multiplying the unit weight  $w_{1,i}$ (kg/item or kg/m) of each type of plastic fishing gear *i* by the quantity or length  $n_{1,i}$  (items or meters) of gear lost during the target period.

$$D_1 = \sum_i w_{1,i} \cdot n_{1,i} \cdots \quad (1)$$

(2) Estimation based on purchasing records and loss rate surveys

This survey focused on squid fishing (floating fishing) and longline fishing. Data on the quantity and length of plastic fishing gear were extracted from purchase records of fishing gear during the fishing season from standard squid fishing and longline fishing operations. The weight of the purchased plastic fishing gear was estimated interviews through with fishing gear manufacturers and actual measurements. Additionally, to investigate the percentage of gear purchased to replace fishing gear lost to the sea during operations, a questionnaire was conducted with 12 squid fishing (floating fishing) fishermen and 31 longline fishermen. The marine plastic fishing gear loss  $D_2$ was estimated using Equation (2), by multiplying the estimated weight  $w_{2,i}$  (kg) of each plastic fishing gear type from purchase records by the percentage  $p_{2,i}(-)$  of purchased gear intended to replace lost gear, as indicated in the survey responses.

$$D_2 = \sum_i w_{2,i} p_{2,i} \cdots (2)$$

(3) Estimation based on interviews with fishermen

This survey targeted medium-scale purse seine fishing, large-scale stationary net fishing, salmon stationary net fishing, gillnet fishing, small-scale bottom trawl fishing, dip net fishing, and basket net fishing operations. The interviews covered aspects related to activity volume, such as the number of operating days and catch volume, as well as details about the fishing method, the types, specifications, quantities, sizes (lengths) of plastic fishing gear that may be lost to the sea, the frequency of losses, and the causes of these losses. For fishing methods that reported minimal gear loss, it was assumed that one set of gear would be lost once every 30 years. To convert the information obtained from the interviews into weight, inquiries were made to fishing gear manufacturers, and actual measurements were conducted. The marine plastic fishing gear loss  $D_3$  (kg) was estimated using Equation (3), by dividing the weight  $m_{3,i}$  (kg) of each type of plastic fishing gear *i* by the average period  $f_{3,i}$ (years) between incidents of gear loss for that type.

$$D_3 = \sum_i m_{3,i} / f_{3,i} \cdots (3)$$

#### 2-2. Estimation of plastic fishing gear loss

First, based on the information on plastic fishing gear used per day of operation obtained from the operational record survey and interview survey, the weight was calculated using the same method as for estimating basic units. The weight of plastic fishing gear used per day of operation was determined by multiplying the weight of plastic gear per set by the number of sets used in a single day. The estimated marine plastic gear loss rate was then calculated by dividing the weight of plastic gear lost per day per fishing operation by the daily usage.

Table 1 shows the survey methods, locations, primary target fish species, operating months or days, recent catch volumes, vessel sizes, and numbers based on interview results for nine types of fishing included in this study. Table 2 displays the main types of fishing gear prone to loss, the reasons behind the loss, and the frequency of occurrences. For net-based fishing methods such as purse seine, stationary net, bottom trawl, gillnet, dip net, and basket net fishing, nets were identified as the main type of gear lost. The main causes were damage to nets from getting caught on reefs and natural events, such as rough seas, leading to gear loss. In contrast, for fishing methods using lines, such as longline, squid fishing, and trolling, lures and lines were the primary gear lost, often due to larger fish biting through the line. The frequency of gear loss was higher for line-based fishing compared to net-based fishing.

The estimated marine plastic gear loss rate per basic unit for the nine types of fishing surveyed is

| No. | Fishery type                             | survey method  | research location  | Survey<br>Period  | Main species of fish to be caught   | Months or days of operation        | haul (catch)<br>of fish |
|-----|--|--|--|---|---|------------------------------------|-------------------------|
| 1   | Purse seine<br>fishing                   | purchasing<br>records<br>interviews                                      | Munakata,<br>Fukuoka   | October<br>2021   | Yellowtail, Mackerel, Horse Mackerel, Blue Mackerel, Round<br>Mackerel          | 9 months (April-December)          | 420t                    |
| 2   | Cat notfishing                           | Internieure  | Tsushima,<br>Nagasaki  | December<br>2022  | Yellowtail, Yellowtail Kingfish, Tuna, Grunt, Squid                             | 300 days (12 months)               | 180t                    |
| 3   | 3 Set-net fishing inte                   |  | Tomakomai,<br>Hokkaido   | January<br>2024   | Salmon, Mackerel  | 45 days (September to<br>November) | 300t                    |
| 4   |  |  | Hakata,<br>Fukuoka   | November<br>2022  | Octopus, Silver Biddy, Flounder, Sea Bass, Shrimp                               | 100 days (April-December)          | 15 t                    |
| 5   |  |  | Tomakomai,<br>Hokkaido   | January<br>2024   | Scallop, Flounder   | 40 days (December to March)        | 32t                     |
| 6   | Bottom trawl<br>fishing                  | interviews   | Tomakomai,<br>Hokkaido   | January<br>2024   | Surf Clam   | 90 days (December - April)         | 11t                     |
| 7   | 7  |  | Mukawa,<br>Hokkaido  | January<br>2024   | Surf Clam, Trough Shell, Sakhalin Surf Clam                                     | ten days                           | 5.0t                    |
| 8   | 8  |  | Mukawa,<br>Hokkaido  | January<br>2024   | Shishamo, Ryukyu Fish, Saffron Cod  | 21 days (October-November)         | 75 t                    |
| 9   | Gillnot fishing                          | interviewe   | Tomakomai,<br>Hokkaido   | January<br>2024   | Alaska Pollock, Atka Mackerel, Sailfin Poacher, Flathead Flounder               | 100 days (October - February)      | 65t                     |
| 10  | 10                                       |  | Tomakomai,<br>Hokkaido   | January<br>2024   | Flounder, Skates, Shark, Cod, Raven Fish  | 38 days (May-July)                 | 8.4t                    |
| 11  | Dip net fishing                          | interviews   | Tsushima,<br>Nagasaki  | December<br>2022  | Black Scraper   | thirty days                        | 4.8t                    |
| 12  | Basket trap fishing<br>(crabs, lobsters) | interviews   | Tomakomai,<br>Hokkaido   | January<br>2024   | Whelk, Spiral Shell   | 110 days (March-October)           | 11t                     |
|     |  | purchasing October<br>records 2021 Time Duffer Security Manhard Plasters |  | Tizer Duffer, Spenish Maskerel, Blackmatted Duffer, Daven | 3 months (January - March)  |                                    |                         |
| 13  | Longline fishing                         | outflow records<br>interviews  | Fish 2023 Fish   |   | twenty-first day of the<br>month  | 1.8t                               |                         |
|     |  | purchasing<br>records  | Munakata   | October<br>2021   |   | 12 months                          | 2.9t                    |
| 14  | Floating fishing                         | outflow records<br>interviews  | records Munakata, 2023 Swordtip Squid, Spanish Mackerel, Yellowtail, Yellows February Yellow Seabream 2023 |   | Sworoup Squid, Spanish Mackerel, Tellowtall, Tellow Grouper,<br>Yellow Seabream | (10 days)                          | (0.35t)                 |
| 15  | Trolling fishing                         | outflow records  | Munakata,<br>Fukuoka   | 2023  | Spanish Mackerel, Yellowtail  | (15days)                           | (0.27t)                 |

Table 1 Details on the fishing gear loss survey

presented in Table 2. The table shows the marine plastic gear loss rate per fishing operation per day and per ton of catch. For fishing types surveyed across multiple operations (stationary net fishing, bottom trawl, and gillnet fishing), the total marine plastic gear loss, catch volume, and activity volume (such as operational days) were summed and then divided by the number of operations surveyed to calculate the average rate.

In terms of marine plastic gear loss per ton of catch, line-based fishing showed a higher loss rate than net-based fishing. Within net-based fishing, gillnet, basket net, and stationary net fishing had relatively high rates. Fishing methods with loss rates exceeding 0.1 kg/t, excluding trolling, shared the common characteristic of gear not being connected to the vessel. These findings led to the categorization of four groups, as illustrated in Figure 1, based on the tendency for gear loss.

The estimated marine plastic gear loss rate per fishing operation per day for the nine types of fishing surveyed is shown in Table 3, which includes the daily plastic gear usage and marine loss rate per fishing operation. For fishing types surveyed across multiple operations (stationary net, bottom trawl, and gillnet fishing), the average values across operations were used.

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|---|---------|
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| 1 abiez. 1 lastie fishing gear loss per basic | / umi   |

| Fishery type         | Plastic outflow per<br>management entity<br>per operating day<br>(kg-plastic gear<br>loss/operating days) | Plastic outflow per 1<br>ton of catch<br>(kg - plastic gear<br>loss/t - catch) |
|----------------------|---|--|
| Purse seine fishing  | 0.16  | 0.073  |
| Fixed-net fishing    | 0.19  | 0.14   |
| Bottom trawl fishing | 0.053   | 0.099  |
| Gillnet fishing      | 0.57  | 1.1  |
| Dip net fishing      | 0.0062  | 0.038  |
| Basket trap fishing  | 0.066   | 0.66   |
| Longline fishing     | 1.5   | 14   |
| Floating fishing     | 0.036   | 1.4  |
| Trolling fishing     | 0.0057  | 0.24   |

Table3. Plastic fishing gear loss rate

| Fishery type         | Plastic fishing gear<br>use per operating day<br>(kg-plastic gear use<br>/operating days) | Plastic loss rate per<br>management entity<br>per operating day<br>(%) |
|----------------------|---|--|
| Set-net fishing      | 5,937   | 0.0019   |
| Bottom trawl fishing | 100   | 0.067  |
| Gillnet fishing      | 1,388   | 0.058  |
| Dip net fishing      | 1,772   | 0.00035  |
| Basket trap fishing  | 416   | 0.016  |
| Longline fishing     | 39  | 3.8  |
| Floating fishing     | 7   | 0.48   |
| Trolling fishing     | 3   | 0.19   |



Fig 1 Grouping of fishing methods based on the likelihood of gear loss

The national marine plastic gear loss volume in Japan was estimated by multiplying the estimated unit rate per ton of catch by the national catch volume for each fishing type. For fishing types not included in the survey, four groups (from Figure 1) were used, applying the average unit rate for each group.

The estimated national marine plastic gear loss volume was approximately 2,507 tons (Table 5). By fishing type, gillnet fishing (144 tons) accounted for the highest loss in net-based fishing, while longline fishing (1,674 tons) had the highest loss in line-based fishing.

| Fishery type                | Amount of fish<br>catch<br>(1,000t) | Amount of plastic fishing gear loss (t) |
|-----------------------------|-------------------------------------|---|
| Bottom trawl fishing        | 673                                 | 67                                      |
| Seine net fishing           | 156                                 | 11                                      |
| Purse seine fishing         | 1,317                               | 96                                      |
| Gillnet fishing             | 134                                 | 144                                     |
| Set-net fishing             | 19                                  | 1                                       |
| Fixed-net fishing           | 436                                 | 61                                      |
| Other net fishing           | 38                                  | 13                                      |
| Longline fishing            | 122                                 | 1,674                                   |
| Pole-and-line fishing       | 97                                  | 23                                      |
| Squid fishing               | 29                                  | 42                                      |
| Trolling fishing            | 11                                  | 3                                       |
| Other types of line fishing | 23                                  | 88                                      |
| Other method of fishing     | 133                                 | 282                                     |
| Total                       | 3,189                               | 2,507                                   |

Table4. Amount of plastic fishing gear loss

# 2-3 Efforts by fishermen and fisheries cooperatives to address plastic gear loss

During interviews, all fishermen emphasized that gear loss was unintentional, and they made their best efforts to prevent it. Particularly with fishing nets, considerable attention was given to avoid damage or loss due to the high replacement cost. Additionally, some municipalities and fisheries cooperatives implemented programs for collecting and reusing fishing nets and ropes. This initiative is considered effective in preventing gear from being abandoned along shorelines and serves as a countermeasure against marine plastic gear loss, contributing to resource recycling.

#### 3. CONCLUSION

The results obtained from this study are summarized as follows:

- The estimated amount of plastic fishing gear lost to the ocean from vessel-based fisheries was 2,507 tons.
- Line-based fishing methods may have a higher probability of plastic fishing gear loss to the ocean compared to net-based fishing.
- Fishing methods where gear is not connected to the fishing vessel have a greater likelihood of plastic fishing gear loss.

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# IN SITU FORMATION OF Ni(OH)2@NF CATHODE ELECTRO FENTON METHOD FOR DEGRADATION OF TETRACYCLINE IN WATER

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#### **1 INTRODUCTION**

Tetracycline (TC) is a broad-spectrum antibiotic naturally produced by specific types of actinomycetes, widely used in medical and livestock fields. However, the complex molecular structure of TC makes it difficult to effectively remove it through traditional biodegradation methods or conventional water treatment measures, resulting in its persistent presence in the environment and potential threat to aquatic ecosystems and human health. In this context, electro Fenton technology has received close attention from researchers in recent years. It generates highly oxidative hydroxyl radicals  $(\cdot OH)$ through electrochemical processes, which can efficiently degrade various difficult to degrade organic pollutants, including TC, and convert them into harmless or low toxic substances. In the electro Fenton system, the selection of cathode materials plays a crucial role in the efficiency of the entire processing process. Among them, foam nickel (NF) is a kind of three-dimensional porous functional material with interconnected pores and metal skeleton. This kind of material has a large electrochemical reaction surface interface and is one of the ideal catalyst support materials. At the same time, it is conducive to mass transfer in the process of degradation reaction, has a way to generate additional H<sub>2</sub>O<sub>2</sub>, has high conductivity, high cycle stability and low cost<sup>[1,2]</sup>, and has great application prospects in electrochemical hydrogen evolution reaction and

oxygen evolution reaction electrode electrocatalytic materials<sup>[3]</sup>. Therefore, this article explores and develops new and efficient cathode materials based on NF, which has crucial strategic significance for promoting the performance leap of electro Fenton technology in treating refractory organic pollutants such as tetracycline.

#### 2 MATERIALS AND METHODS

#### 2.1 Preparation of Ni(OH)2@NF material

Firstly, cut the 3D NF sheet into a size of 2 cm×2 cm, and ultrasonically clean it in 0.1 mM dilute sulfuric acid for 20 minutes. Then ultrasonically clean it in anhydrous ethanol and deionized water for 20 and 15 minutes, respectively, to obtain a clean 3D NF sheet and place it in a 100 mL PTFE liner. Add different qualities of urea and 80 ml of deionized water into a beaker, stir magnetically for 30 minutes to form a precursor solution. Add the precursor solution into the PTFE lining. Seal the hot liquid container and treat it in an oven at 160 °C for 6 hours. After natural cooling to room temperature, remove it and rinse the material with ultrapure water. Then dry it at 60 °C to obtain Ni(OH)<sub>2</sub>@NF material. The material preparation process diagram is shown in Figure 1.

#### 2.2 Catalytic performance experiment

The degradation experiment using TC as a pollutant is as follows: 80 mL of TC solution and Na<sub>2</sub>SO<sub>4</sub> are placed in a reactor and mixed with magnetic stirring. Using Ni(OH)<sub>2</sub>@NF as the cathode, ruthenium iridium titanium plate(DSA) as the anode, Na<sub>2</sub>SO<sub>4</sub> as the electrolyte solution, connect the electrodes, and take about 1 mL of the solution with a syringe at specified time intervals (0, 5, 10, 20, 30, 60 min), then filter it



Figure. 1. Material preparation process diagram

## **3 RESULTS AND DISCUSSION**

#### 3.1 Urea addition amount

As the hydrothermal temperature gradually increases, urea will gradually decompose, creating alkaline conditions for the solution. The metal cations (Ni<sup>2+</sup>) in the solution react with OH<sup>-</sup> to form Ni(OH)<sub>2</sub> precipitates, which adhere to the surface of NF and further grow into sheet-like structures due to the intrinsic crystallization characteristics of the product<sup>[4]</sup>. To investigate the effect of urea addition on TC degradation, different addition amounts of 0, 0.01, 0.02, 0.03, 0.04, 005, 0.06, and 0.07 mol/L were set for comparison, while other experimental conditions were the same. From Figure 4, it can be seen that with the increase of urea concentration, the degradation efficiency of TC by the cathode material gradually increases. The degradation rate reaches its maximum at a concentration of 0.05 mol/L, which is 64.0%. Compared with pure NF (44.6%), the degradation rate has increased by 1.45 times. Pure NF and NF with urea addition of 0.05mol/L are shown in Figure 3. When the urea concentration increased to 0.06 mol/L, the degradation rate did not show а significant improvement, so the urea addition amount was chosen as 0.05 mol/L for this experiment.

through a 0.22  $\mu$ m filter membrane. Add the filtered solution to a colorimetric tube and dilute 5 times. Measure the absorbance at the maximum absorption wavelength of 357 nm using a UV visible spectrophotometer. The experimental setup diagram is shown in Figure 2.



Figure. 2. Experimental setup diagram







Figure. 4. The effect of different urea addition amounts

on TC degradation

#### 3.2 Electrolyte concentration

Adding electrolytes is often used to increase the conductivity of organic solutions. This article uses Na<sub>2</sub>SO<sub>4</sub> as the electrolyte, which has stable chemical properties and is therefore used as a conductive medium in many experiments<sup>[5]</sup>. The electrolyte concentration will have a certain impact on the electro Fenton system. This article sets different electrolyte concentrations of 5, 10, 15, and 20 mM for comparison, and other experimental conditions are the same. As shown in Figure 5 (a), under the same conditions, the degradation rate decreases with the increase of electrolyte concentration. When the electrolyte concentration is 10 mM, the degradation rate is the highest at 64.0%. When the electrolyte concentration is greater than 10 mM, the excessive number of inorganic ions will compete with organic matter, affecting the efficiency of electron transfer and reducing the yield of ·OH, resulting in a decrease in degradation rate. Therefore, an electrolyte concentration of 10 mM was chosen for this experiment.



Figure. 5. The effects of different influencing factors on

TC degradation: (a) electrolyte concentration; (b) current density; (c) initial concentration; (d)pH

#### 3.3 Current density

The function of the reaction current is to provide

electrons for the reduction of O<sub>2</sub> to generate H<sub>2</sub>O<sub>2</sub>, which has a certain impact on the electro Fenton system. To investigate the effect of current density on TC degradation, different current values of 5, 10, 15, 20, 25, and 30 mA/cm<sup>2</sup> were set for comparison, while other experimental conditions were the same. According to Figure 5 (b), under the same conditions, the higher the current density, the higher the TC degradation rate. Increasing the current can accelerate the electron transfer rate of the reaction and effectively promote the generation of H<sub>2</sub>O<sub>2</sub>, thereby increasing the amount of ·OH<sup>[6]</sup>. Within 60 minutes, when the current density is 25 mA/cm<sup>2</sup>, the degradation rate can reach up to 78.5%. Increasing the current density by 5 mA/cm<sup>2</sup> does not significantly improve the degradation rate. Considering current efficiency and practical applications in the later stage, the optimal current density for the reaction is selected as 25 mA/cm<sup>2</sup>.

#### 3.4 Initial concentration

To investigate the effect of initial concentration on TC degradation, different concentrations of 5, 10, 15, 20, and 25 mg/L were set for comparison, while other experimental conditions were the same. As shown in Figure 5 (c), as the initial concentration of TC increases, the degradation efficiency of TC gradually decreases. At an initial concentration of 5 mg/L, the degradation rate can reach up to 81.1%, and at 10 mg/L, it can reach 78.6%. This is because as the initial concentration increases, the possibility of reaction between simulated pollutant molecules and active substances decreases. applications Considering practical and future development, the initial concentration of TC is chosen to be 10 mg/L.

#### <u>3.5 pH</u>

The pH of the solution not only has a significant impact on the characteristics of  $TC^{[7]}$ , but also affects the amount of  $H_2O_2$  generated. Therefore, different solution pH values of 3, 4.94 (unadjusted), 7, 9, and 11 were set to study the effect of pH on the degradation of TC by the electro Fenton system, while other experimental conditions were the same. According to Figure 5 (d), under the same conditions, the degradation rate is higher when the pH is relatively neutral. When the pH is not adjusted (4.94), the degradation rate reaches the highest of 78.6%. When the solution is in strong acidity, it can cause ion leaching of active components, directly affecting the stability of the catalyst; Under alkaline conditions, the generated oxygen can be reduced to hydrogen peroxide ions, reducing the degradation efficiency<sup>[8]</sup>. Considering economic factors, we chose not to adjust the pH.

#### **4 CONCLUSION**

This article describes the in-situ formation of Ni(OH)<sub>2</sub> nanostructures on NF substrate using hydrothermal method, and the construction of Ni(OH)<sub>2</sub>@NF cathode. The experimental results showed that the cathode exhibited excellent electrocatalytic activity in the electrochemical degradation process. Under the conditions of urea dosage of 0.05 mol/L, electrolyte concentration of 10 mM, current density of 25 mA/cm<sup>2</sup>, and no pH adjustment, the Ni(OH)2@NF cathode could achieve a degradation rate of over 70% for tetracycline wastewater below 15 mg/L. Compared with pure NF (44.6%), it had significant degradation effect, providing a new idea and approach for efficient removal of tetracycline in water, which has important theoretical significance and practical application value.

#### ACKNOWLEGEMENT

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## STUDY ON THE EFFECT OF BIOLOGICAL DRYING TECHNOLOGY ON THE RESOURCE UTILIZATION OF COW MANURE AND BIOGAS RESIDUE

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#### ABSTRACT

This study aims to utilize biodrying technology to treat deeply anaerobic cow manure digestate, with the objectives of reducing its biological toxicity and achieving rapid humification. The physicochemical properties of the cow manure digestate were analyzed, and it was determined that sawdust and corn cob would serve as the conditioning agents for biodrying. When the blending ratio of digestate, sawdust, and corn cob was 20:2.5:3.5, the moisture content of the digestate was around 72%. After adding a compound thermophilic microbial inoculant, the biodried product exhibited the lowest phytotoxicity and the highest degree of humification. Among the eight control groups, the mixed substrate with inoculant group (C7) showed a material temperature exceeding the auxiliary temperature (52.7°C) within 6 days, entering the high-temperature phase. The rate of moisture removal accelerated, reducing the moisture content to below 30% within 10 days, and the seed germination index reached 93%. The final biodried product met the standards for biological organic fertilizer.

#### **1 INTRODUCTION**

The cow manure biogas residue is the product of anaerobic fermentation of fresh cow manure, which is rich in nutrients and has a high content of refractory organic matter. However, its high water content, high phytotoxicity, and abundant anaerobic microbial community limit the direct application of cow manure biogas residue to the field (Zainab A. B. Al-Hafidh and Ayman Albanna, 2023). Zheng Wei et al. summarized the characteristics of anaerobic biogas residues from various organic wastes in their paper "A Brief Analysis of Composting Parameters for Anaerobic Biogas Residues from Organic Wastes". They mentioned that the water content of cow manure biogas residue is typically around 80%, with a C/N ratio generally below 15, and a seed germination index below 40%. This type of biogas residue from livestock and poultry manure is difficult to utilize as a resource (Ben et al., 2018). Using traditional composting technology for secondary aerobic fermentation of cow manure biogas residue is challenging. It not only requires a large amount of external conditioners to adjust the C/N ratio, which increases composting costs, but also has a low aeration rate, resulting in a long composting cycle. Additionally, localized anaerobic conditions can easily occur, affecting the composting effect (Savarino et al., 2020). To overcome these challenges, researchers and practitioners are exploring alternative composting methods and technologies that can more effectively utilize cow manure biogas residue. For example, biodrying technology, which involves the use of microorganisms to reduce the water content of the residue, may be a promising approach. Additionally, the use of advanced composting reactors and optimization of composting parameters can also improve the composting efficiency and quality of cow manure biogas residue
(Hanna et al., 2018). The biodrying technology derived from aerobic fermentation has achieved good application results in municipal sludge and organic waste (Li et al., 2012). Biodrying utilizes high ventilation and elevated auxiliary temperatures to shorten the fermentation period, accelerate the humification process, and improve resource recovery efficiency. Xu Mingyue conducted a study on the simultaneous treatment of high-moisture food waste using biodrying and aerobic composting processes. The results showed that biodrying achieved well-matured products with a moisture content below 30% in a relatively short period of time, and the greenhouse gas emissions were significantly lower than those from aerobic composting treatment(Dahshan et al., 2015). Ma Jiao conducted a study on the combined conditioning and thermally-assisted biodrying of highmoisture urban organic waste. The results showed that high-temperature-assisted biodrying can significantly accelerate the humification process of organic matter, and the product obtained has a higher degree of humification compared to traditional drying methods(Cai et al., 2019). Overall, the utilization of cow manure biogas residue as a resource requires further research and development of effective composting technologies and methods to overcome its high water content, low C/N ratio, and high phytotoxicity. Based on the experiences of predecessors, this study intends to adopt biodrying technology to treat deeply anaerobic cow manure biogas residue, determine the feasibility of biodrying for high-moisture cow manure biogas residue, explore the effects of different conditioners and exogenous microbial inoculants on the biodrying of biogas residue, and clarify the feasibility and effectiveness of biodrying for the resource utilization of cow manure biogas residue.

## 2 MATERIALS AND METHODS

#### 2.1 Preparation of materials and reactor

Feasibility study on biodrying of cow manure biogas residue. The reactor is of laboratory scale, as shown in Figure 1. The device includes a pump, a gas flow meter (LZB-3, 0.1~1.0 L/min), a biodrying reactor, and a gas

absorption bottle. The biodrying reactor consists of a biodrying tank, a temperature detector, inlet and outlet ports, a constant temperature water bath, and a controller. Each fermentation tank is filled with approximately 1.0 kg of wet biogas residue. The external conditioners used are wood chips and corn cobs, both crushed to a diameter of 5mm before addition. The external inoculant is a thermophilic microbial inoculant prepared in the laboratory, mainly consisting of bacteria, actinomycetes, fungi, and yeast. It is cultivated in LB medium at 60°C for 48 hours and added at a concentration of 0.5%. The auxiliary heating temperature for biodrying is set at 50°C, and the ventilation rate is 0.5 L/(min kg), which ensures that the thermophilic microorganisms can quickly adapt to the environment within the system and carry out metabolic activities, favoring the rapid initiation of biodrying.



Figure-1: Laboratory-scale biodrying reactor

Conditioners are necessary additives in the biodrying process. In this study, wood chips and corn cobs are used as conditioners for biodrying. The advantages of these materials are their low cost, easy availability, and their ability to regulate the internal environment of the biogas residue during drying when mixed with it, thereby creating favorable initial conditions for drying.

Prior to the start of the drying process, the initial physicochemical properties of the biogas residue and conditioners were investigated. The basic physicochemical properties of the biogas residue and conditioners are shown in Table 1.

| Physicochemical properties | Cow dung digestate             | sawdust                         | Corn cob   |
|----------------------------|--------------------------------|---------------------------------|------------|
| pH                         | 8.21 ± 0.06 6.62±0.04          |                                 | 8.03±0.07  |
| water content (%)          | $80.13 \pm 0.04$ 2.7 $\pm 0.1$ |                                 | 5.99±0.3   |
| C (%, d.s.)                | $37.08\pm 0.3$                 | $37.08 \pm 0.3$ $51.83 \pm 0.1$ |            |
| N (%, d.s.)                | $3.53 \pm 0.2$ $0.31 \pm 0.04$ |                                 | 0.36±0.01  |
| C/N( d.s.)                 | $10.52\pm0.4$                  | 166.72±0.4                      | 133.19±0.2 |
| VS/TS (%, d.s.)            | $63.19 \pm 0.03$               | 1                               | /          |
| EC(µs/cm)                  | $808\pm11$                     | 1                               | /          |
| TOC (mg/g)                 | $28.844\pm0.05$                | 1                               | /          |
| GI (%)                     | $39.5\pm5.0$                   | 1                               | /          |

Table-1: Basic physicochemical properties of cow manure biogas residue, wood chips, and corn cobs.

#### 2.2 Experiment design

To determine the optimal conditioning scheme for biodrying of cow manure biogas residue, this study set up four control groups for combined conditioning and drying of the biogas residue, using wood chips and corn cobs as conditioners, with the control condition of adjusting the moisture content of the material to around 70%. Additionally, to explore the impact of exogenous inoculants on the biodrying process, four more control groups with added inoculants were included based on the original setup. Therefore, a total of eight control experiments were conducted in the feasibility study of biodrying of cow manure biogas residue, with a drying period of 12 days. Changes in the physicochemical properties of the material during the drying process were monitored to determine the best biogas residue drying scheme. The control group treatments are shown in Table 2. The impact of exogenous inoculants on biodrying, as revealed by literature research, cannot be ignored. They influence the microbial community structure and metabolism in the material environment. thereby accelerating the biodrying process and promoting the humification process.

Table-2: Eight treatment methods for the control groups in the feasibility study of biodrying experiments.

| Control treatment | Digestate/g | sawdust/g | Corn cob/g | Thermophage/ml | Initial moisture content |
|-------------------|-------------|-----------|------------|----------------|--------------------------|
| CK                | 1000        | 1         | /          | /              | 80.16%                   |
| C1                | 1000        | /         | /          | 1.5%, 15ml     | 81.25%                   |
|                   |             |           |            |                |                          |
| C2                | 1000        | 185       | /          | /              | 72.06%                   |
| C3                | 1000        | 185       | /          | 1.5%, 15ml     | 72 449/                  |
|                   |             |           |            |                | /3.44%                   |
| C4                | 1000        | /         | 250        | /              | 72.91%                   |
| C5                | 1000        | /         | 250        | 1.5% 15ml      |                          |
|                   |             |           |            | 1070, 1011     | 73.45%                   |
| 6                 | 1000        | 125       | 175        | /              | 72.15%                   |
| 0                 | 1000        | 125       | 175        | ,              | 12.1370                  |
| C7                | 1000        | 125       | 175        | 1.5%, 15ml     | 73.47%                   |
|                   |             |           |            |                |                          |

#### **3 RESULTS AND DISCUSSION**

# <u>Changes in moisture content of each control group</u> during the drying process.

When the drying cycle is 12 days, among the four groups of CK, C2, C4, and C6 with sterile agents and externally connected C-source conditioning agents, only the C6 group (a mixture of sawdust and corncob) has a moisture content below 30% on the 11th day, with a moisture content of 27.11%. Compared with the blank control group CK, the moisture content of the control groups with added conditioning agents decreased more significantly. The specific pattern is as follows: mixed group > sawdust group > corncob group, as shown in Figure 2 (a). This indicates that the addition of conditioning agents optimizes the drying effect of cow manure biogas residue.

For the control groups inoculated with exogenous microbial agents,  $C3 \ C5 \ and C7 \ the moisture content decreased to below or close to 30% at the end of the drying process. Specifically, the moisture content of the C7 group had already dropped to 25.51% on the 10th day; the moisture content of the C5 group decreased to 29.88% on the 12th day; and the moisture content of the C3 group was close to 30%, at 30.88%. The details are shown in Figure 2 (b). This indicates that the addition of exogenous microbial agents accelerated the removal of$ 

moisture from the biogas residue, possibly due to changes in the microbial community structure and metabolism.



Figure-2: Changes in moisture content of the control groups. (a)Moisture changes in the conditioner control groups.;(b)Moisture changes in the control groups with exogenous microbial inoculants.

A unified analysis of the eight control treatments is shown in Figure-3 and Figure-4. It is not difficult to observe that the C7 group, which combined conditioning agents with exogenous microbial inoculants, achieved the best drying effect, with a high moisture reduction value and a significant moisture removal rate. On the 5th day, the temperature of the C7 group exceeded the auxiliary temperature, reaching 52.7°C, entering the high-temperature and composting phase. It met the moisture drying standard within 10 days, with a moisture removal rate as high as 4.8%/d.



Figure-3: (a) Comparison of materials after the completion of drying process. (b) Changes in moisture content of the 8 experimental treatment groups.



Figure-4: Moisture removal values and average moisture removal rates of the 8 control treatment groups.

### **4 CONCUSION**

Biological drying treatment of cow manure biogas residue with high moisture content is feasible. Based on the moisture content indicator to evaluate the drying effect of different treatment groups, the mixed conditioner plus inoculant treatment group achieved the ideal drying value within 10 days, demonstrating the lowest time cost. Although the low C/N ratio of biogas residue may limit the duration and effectiveness of composting fermentation, resulting in lower fertilizer value of the dried product, the product after drying treatment can still be used as organic soil for landscaping. This indicates that biological drying technology has good development and application prospects in the treatment of biogas residue.

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