

Formation of Unknown Ozonation By-Products in Flocculated Nanofiltration Leachate Concentrates Treated by O₃ and UV/O₃ Systems: Characteristics and Mechanisms



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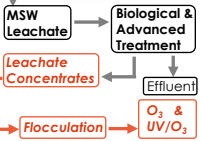
CHEN Weiming, LIU Dan
Faculty of Geosciences and Environmental Engineering
Southwest Jiaotong University, Chengdu, China

INTRODUCTION



Production of leachate concentrates

- Its production is inevitable due to the vast application of membrane separation technology in leachate treatment
- It enriched many recalcitrant organic matter from leachate and featured with high level of unsaturation and aromaticity

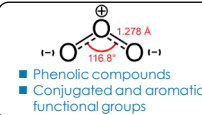


Reactivity of O₃ towards aromatic matter

- O₃ preferentially reacts with highly unsaturated and aromatic organic matter
- Due to the preferential reactivity, O₃-based system has been applied for the treatment of leachate concentrates

Unknown ozonation by-products formed in O₃-based systems

- Recent studies have shown that treating organic wastewater streams with O₃ can generate ozonation by-products (OBPs) with complex or even unknown components
- The newly generated polar oxygen-containing OBPs are even more toxic than their parent pollutants



OBJECTIVES

- Characterize OBPs using ESI FT-ICR MS
- Study the effect of HO· reaction (UV/O₃) on OBPs
- Investigate the formation mechanism of OBPs in O₃ and UV/O₃ systems

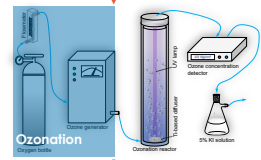
Methodology



1. Sampling—NF concentrates

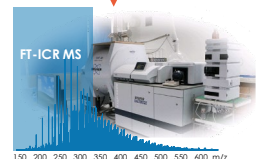
Water Quality

- pH value of 7.83;
- TOC of 1,044 mg/L;
- UV₂₅₄ of 34.7 cm⁻¹;
- SUVA₂₅₄ of 3.324 L/(mg·m);
- CN of 1.598 cm⁻¹



2. Flocculated NFC preparation

- Polyferric Sulfate (PFS) with a 7.5 g/L was used to pretreat the NFC and to produce the flocculated NFC (FNFC)



3. O₃ and UV/O₃ reactions

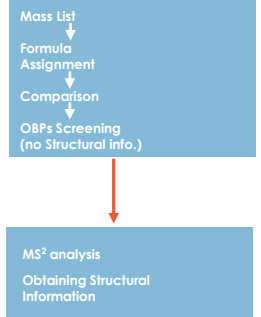
- O₃: 13.35, 21.80, 40.61, and 54.40 mg/min
- UV lamp: 10 W, 253.7 nm
- Reaction time: 60 min

4. ESI FT-ICR MS analysis

- Instrument: Bruker Apex ultra FT-ICR MS with 9.4 T
- Pretreatment (SPE-DOM)
- Electrospray mode: Negative
- Formula Assignment (An in-house software)
- Molecular Descriptor Calculation (H/C; O/C; DBE; NOSC; AI_{mod} ; Xc; KMD; etc.)

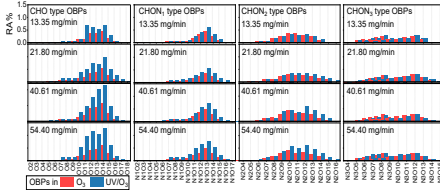
5. Identification of Unknown OBPs by MS²

- Instrument: Orbitrap MSMS (Orbitrap Fusion MS)
- Electrospray mode: Negative
- Resolution: 500,000 at m/z 400
- Software: Thermo Xcalibur Qual Browser etc.



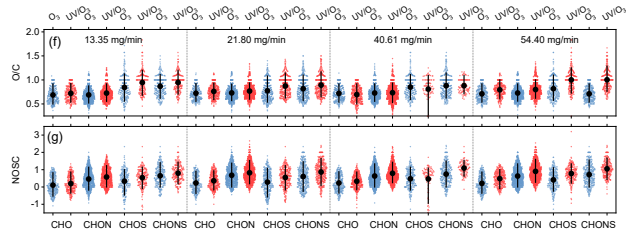
RESULTS

Major OBPs



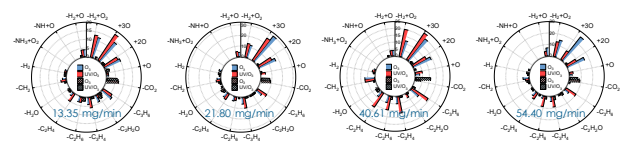
- O₃ and HO· greatly changed molecular composition of FNFC
- Many highly oxidized compounds were produced
- CHO and CHON are major OBPs

Characteristics of OBPs



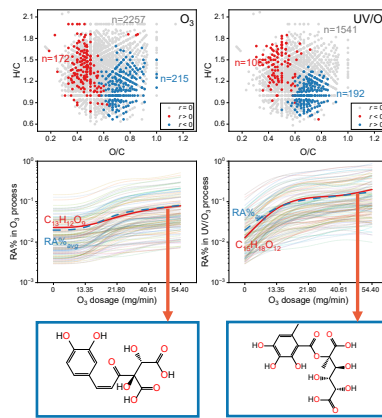
- Higher molecular weight (more O functional groups) under low O₃/HO· action
- Much Lower molecular weight (smaller carbon bone) under high O₃/HO· action

OBPs Formation Pathways

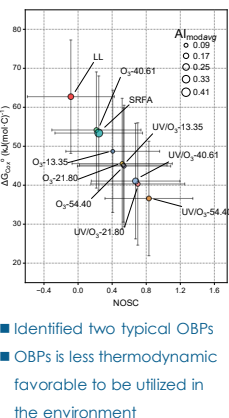


- "Precursor-OBPs" linkage analysis
- Methyl/amine to Carboxyl/nitro (-H₂+2O)
- Tri(Di)oxygenation (+3/2O)
- Decyclopropyl (-C₃H₄)
- Oxidative deamination (-NH₃+2O)
- Deisopropyl (-C₃H₆)

Identified OBPs markers



Environmental Impact



- Identified two typical OBPs
- OBPs is less thermodynamic favorable to be utilized in the environment

CONCLUSION

- CHO and CHON compounds are the main components of OBPs via oxygenation reactions, demethylation reactions, oxidative deamination reactions
- Properties of OBPs varies and depends on the action strength of O₃ and HO·
- Structures of typical OBPs were identified by MS²
- OBPs have a ΔG_{ox}° even lower than that natural fulvic acid
- OBPs are difficult to convert to less harmful materials, and their environmental behavior and fate should be the focus of future studies