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DOCTORAL THESIS

Transformation chemistry and environmental fate of emerging contaminants under advanced oxidation processes

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Abstract

Emerging contaminants (ECs) are group of chemicals that widely appeared in the aquatic and terrestrial environments. Due to its ambiguous fate and potential risk to the ecosystem and/or human health, ECs have received much attention to scientists in recent years. Although numerous works have been done, information on the fate of emerging contaminants and impact to the environment are still limited.

Artificial sweeteners – acesulfame (ACE) was recently recognized as EC because of its persistence and ubiquitous occurrence in the worldwide environment. Although ACE is safe for human consumption, research on the fate of ACE and potential risk to the environment was scarce. Recently, ACE by-products derived from photolysis/photocatalysis, chlorination and permanganate oxidation were reported that have shown higher toxicity than precursors. Some of its byproducts are potential carcinogens. Alternative advanced oxidation processes (AOPs) for safe removal of ACE from contaminated water and investigation of its transformation pathways are urgently demanded.

To fill this research gap, the transformation and the changes in toxicity of ACE under peroxone (O_3/H_2O_2) process were firstly studied in this work. ACE was effectively degraded through hydroxyl radicals (HO•) derived from peroxone process. Degradation of ACE under peroxone process with different influential

parameters was systematically studied. Transformation products (TPs) of ACE were identified through ultra-high performance liquid chromatography – quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS). Molecular structures of four new identified TPs were tentatively proposed according to the mass measurements with high accuracy and fragments generated from MS/MS. The declined toxicity compared to conventional treatments of ACE was probably owing to difference in transformation chemistry and generation of different TPs. Peroxone process demonstrates to be a promising treatment for safe removal of ACE.

However, unreacted hydrogen peroxide (H_2O_2) released to the environment that may become a potential threat to biota, which is the drawback of H_2O_2-based AOPs. UV/chlor(am)ination are emerging AOPs for replacing conventional UV/H_2O_2. Degradation of ACE under UV/chlor(am)ination were then investigated. The major reactive species for ACE degradation under UV/chlor(am)ination were UV irradiation, HO• and reactive chlorine species (RCS). Transformation pathways under different treatments were systematically compared. The differences in ACE TPs formation among treatments were due to different reactive species generated in the reaction. Toxicity results revealed that TPs in UV/chlor(am)ination had higher toxicity compared to other treatments.

Permanganate/bisulfite (PM/BS) is a novel AOPs that can degrade a broad

range of ECs at extraordinary high rate. The degradability of PM/BS process towards different representative types of compounds was further studied by investigating the kinetics, reaction site specificity and transformation chemistry. ACE and carbamazepine (CBZ) are typical olefinic compounds. Sucralose (SUC) was selected as a representative compound that without aromatic and olefinic moieties. Preferred reaction sites of Mn^{3+} species were elucidated by identification of the TPs with UHPLC-QTOF-MS. Cleavage of olefinic bonds was the main reaction mechanism of PM/BS process. Chemical structures containing electron-donating groups also preferentially reacted with electrophilic Mn^{3+} species during the process. In addition, degradation of ACE during PM/BS process did not induce higher toxicity. General prediction rules for PM/BS process towards degradation of organic contaminants were proposed.

In summary, this work presents several AOPs for degradation of ACE in water, presenting direction for further study to develop new treatment processes for ACE and other ECs which would yield higher toxicity by-products in traditional degradation at water treatment facilities.

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