Emerging Contaminants: Environmental Fate of Artificial Sweeteners

JIANG Yanan

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Principal Supervisor: Dr. Kelvin S. Y. Leung

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Abstract

Artificial sweeteners (AS) have been defined as the newest emerging contaminants accumulated in aquatic environment. Four AS (acesulfame, saccharin, cyclamate, sucralose) samples in thirteen locations collected from surface sea waters in Hong Kong were analyzed using Ultra performance liquid chromatography-electrospray ionization-triple quadrupole Mass Spectrometry, which analytical method was developed in this study. Water samples were pretreated and cleaned-up by a Strata-X 33 µm Polymetric RP extraction cartridges during matrix-match standard addition SPE procedure. The calibration curve exhibited a linear dynamic range from 0.05 to 1 µg L\(^{-1}\) including sample blank with correlation coefficient > 0.9975. The recoveries of AS were ranged from 70% to 125% in standard addition method at different concentration ranges from 0.06 to 1 µg L\(^{-1}\). The method limit of detection and limit of quantification was 0.006 and 0.1 µg L\(^{-1}\), respectively, and the relative standard deviations (n = 5) were less than 9.2%. The method was successfully applied to analyze water samples collected from surface sea water at a wide range of various concentrations. In our work, the highest concentration of acesulfame was up to 0.38 µg L\(^{-1}\) and 0.30 µg L\(^{-1}\) in summer and winter, respectively. Levels of saccharin and cyclamate were lower than 0.26 µg L\(^{-1}\). Sucralose detected was mostly below quantification limit. The highest concentrations were centralized in Victoria Harbor due to high human activities. AS have been confirmed to be highly persistent due to the presence of AS in all sampling locations from east to west in surface sea water in Hong Kong. The aquatic system could be affected by their persistent properties in relation to their bioaccumulation, high
solubility and low adsorbability to solids. Thus, AS could play a potential tracer role and act as an indicator of human activities.

Determination of photo-transformation products during the lab-simulation of advanced oxidation process (AOP) under UV/TiO$_2$ irradiation for four AS using UPLC-Xevo TQ-MS, UPLC-QqQ-MS, and GC-MS was carried out to investigate the mechanisms and pathways of degradation, identification of photo-transformation products, and conditions that affected the processes of degradation. The photo-degradation experiments were conducted in a UV reactor where TiO$_2$ was used as a catalyst. Photo-transformation reactions in two sets of experiments with sample to catalyst ratio of 1:10 and 1:20 respectively, were performed at room temperature.

For the degradation of saccharin, its 2-sulfamoylbenzoic acid, 2-sulfobenzoic acid, catechol 1,2-dioxygenase, SAC AOP 199 were detected with three degradation pathways proposed. For the degradation of sucralose, eight transformation products namely: 1,6-dichloro-1,6-dideoxyfructose, 4-chloro-4-deoxygalactose combined with acetic acid, SUC AOP 457, SUC AOP 413, SUC AOP 431, SUC AOP 395, SUC AOP 457, SUC AOP 450 were detected with three transformation pathways proposed. Three transformation compounds including amidosulfonic acid, cyclohexanone and an unknown compound CYC AOP 195 were detected with a degradation pathway was proposed for cyclamate. Acesulfame was converted to largest number of transformation products during AOP with eight compounds being detected (acetoacetamide-N-sulfonic acid, ACE AOP 196, ACE AOP 214, ACE AOP 170, ACE AOP 152, ACE AOP 124, ACE AOP 97, ACE AOP 96), with a complicated degradation pathway proposed. Based on the data obtained from this research compared with findings reported in the literature, some new pathways of structural transformation during degradation process were
primarily proposed. The lab-simulation experiments also confirm that there is possibility for AS transformed into by-products in the real aquatic environment under solar irradiation or during the WWTP treatment.

Acesulfame showed its most persistent properties and highest concentrations among all the AS in the aquatic environment. During the lab-simulation of AOP, several transformation products formed under UV/TiO$_2$ irradiation. After isolation and collection of the by-products using HPLC-UV combined with a fraction collector, the toxicity of acesulfame and its transformation products were evaluated using Vibrio fischeri. According to the toxicity categories based on the EC$_{50}$ values which are established in legislation (Directive 93/67EEC), the preliminary results of this work showed that acesulfame was not harmful to aquatic organisms since its EC$_{50}$ was 98793 mg L$^{-1}$ and 69230 mg L$^{-1}$ in 5 min and 15 min incubation, respectively. The EC$_{50}$ values of transformation products (EC$_{50}$ = 149 mg L$^{-1}$ and 164 mg L$^{-1}$ in 5 and 15 min incubation, respectively) also displayed no harm to aquatic organisms. However, the toxicity of transformation products increased almost 660 times compared to the toxicity of acesulfame. This confirmed that the degradates may cause adverse effects on ecosystem and human health. If a large amount of acesulfame in the aquatic environment is transformed into toxic compounds under sunlight irradiation or during the WWTP treatment, these transformation products could be harmful to aquatic organisms and may be accumulated in their tissues or cells due to high solubility of transformation products in water. After biological magnification, these harmful compounds may finally enter human body through a biological food chain. The results of lab-simulation of AOP and toxicity thus give a warning to us to avoid underestimating the real environmental consequences.
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