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Degradation pathways and organic matter transformation of acesulfame potassium electro-oxidation in real water matrices

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ABSTRACT

This paper presents the pathways of acesulfame potassium (ACE-K) electro-degradation on a boron-doped diamond (BDD) electrode and the removal/mineralization of ACE-K in different environmental water matrices (biologically treated (hospital) wastewater (BTW), river water (RW), and ground water (GW)). The ACE-K was initially electrochemically transformed to an unknown compound ($m/z = 196$) and then organic acids and inorganic compounds before mineralization. In the water matrices, ACE-K was completely degraded (pseudo-first-order apparent rate constants = $(1.22–2.25) \times 10^{-3}$ s^{-1}). Before electrolysis, all ACE-K spiked solutions showed aromaticity ($SUVA_{254}$), while during electrolysis the variation of aromaticity was consistent with that of total organic carbon removal. The spike of ACE-K covered or lowered the intensities of fluorescence excitation-emission peaks in humic acid-like, aromatic protein I, and fulvic acid-like regions for BTW and those in soluble microbial by-product-like and tyrosine regions for RW and GW. After 120 min electrolysis, the ACE-K-associated fluorescence peaks disappeared but the original dissolved organic matter (DOM)-related ones slightly remained, so the removal/mineralization was harder for the DOM than for the ACE-K in the tested matrices. Electrolysis or spiking ACE-K increased the Microtox acute toxicity response in BTW.

1. Introduction

Artificial sweeteners are widely used in the world. However, their presence in the environment has been an important environmental concern over the past decade because they are recognized as emerging contaminants (or contaminants of emerging concern) in the environment [1]. Acesulfame (ACE) (or its potassium form (ACE-K)), one of artificial sweeteners, is frequently detected in water bodies (*e.g.*). ACE has been detected in relatively high concentration among emerging contaminants in environmental waters such as 10–2500 μg/L in wastewater [2], 3–730 μg/L in groundwater [3], 3.5–780 ng/L in surface water [3], and up to 0.76 μg/L in drinking water [4]. ACE is very resistant to biodegradation in wastewater treatment plants [5] and has high water solubility and low partition coefficient to be used as a wastewater marker [1], so the ACE in environmental waters is usually from wastewater effluent discharge [3]. Due to potential adverse health effects to human [1], ACE is recently concerned for its removal or decomposition into harmless substances in water or municipal wastewater treatment.

The degradations of ACE have been studied using various methods. ACE was found to be poorly removed in conventional multi-barrier drinking water treatment [4], while better removal efficiencies were observed in advanced oxidation processes (AOPs) such as ozone [6] or photo (UV)-based AOP [5, 7]. Another more efficient hydroxyl radical-based AOP for ACE degradation is electrochemical oxidation using boron-doped diamond (BDD) electrodes. In our earlier work, the biodegradation-resistant ACE was found to be completely degraded and its degradation intermediates could be fully mineralized in some water matrices, including secondary biologically treated municipal wastewater [8]. To our knowledge, however, the degradation intermediates and pathways of ACE in electro-degradation are not known yet.

The dissolved organic matter (DOM), a mixture of various organic compounds with different physical and chemical properties, is widely spread in natural environment [9]. Through the characterization by fluorescence excitation-emission matrix (EEM) spectrophotometry, DOM fractions can be categorized in terms of carbohydrates, proteins, humic acids, and fulvic acids [10]. In real environmental aqueous matrices such as surface waters, groundwater, and municipal wastewater, the effect of dissolved organic matter (DOM) on ACE-K degradation must be considered, because DOM might compete with ACE-K for oxidation in the electrochemical degradation process. Therefore, it is also interesting to explore the transformation of DOM during the electrochemical degradation of ACE-K in real water samples, based on the evaluation of fluorescence indices of huminication and autotrophic productivity

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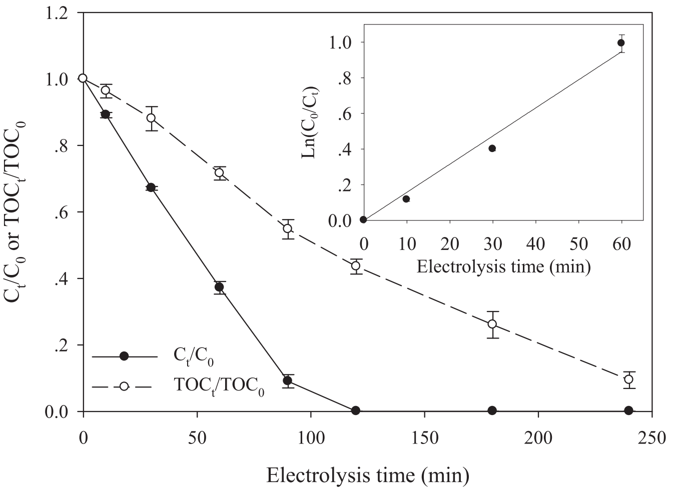

Fig. 1. Variations of ACE-K degradation (solid circle) and TOC removal (open circle) curves with time for ACE-K electrolysis ($C_0 = 1000$ mg/L) in 1 M Na_2SO_4 (inset: $\ln(C_0/C_t)$ against time).

derived from the fluorescence spectroscopic analysis. However, no literature is available for DOM destruction and its influence on ACE-K electrochemical degradation. In this study, we aim at the degradation and mineralization of ACE-K in aqueous solution by electrochemical oxidation on a BDD anode. The degradation intermediates of ACE-K were identified and its degradation pathways were proposed. The mechanisms of DOM transformation during ACE-K electro-degradation in real environmental aqueous matrices were compared. For the reliable analyses of ACE-K and its degradation intermediates in this study, the concentrations of ACE-K greater than those of real environmental waters were adopted to study the degradation kinetics and intermediates of ACE-K [7].

2. Materials and methods

2.1. Chemicals

Acesulfame potassium (ACE-K, $C_4H_4KNO_4S$) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). The ACE-K solution was prepared by dissolving ACE-K in supporting electrolyte. Sodium sulfate, sodium chloride, and trisodium phosphate (12-water) chemicals were obtained from SHOWA Co., Ltd. (Japan). Acetonitrile (HPLC grade solvent), phosphoric acid (65%) and sulfuric acid (analytical grade) were supplied from ECHO Chemical Co., Ltd. (Taiwan), Scharlau (Spain), and AENCORE Chemical Co., Ltd. (Australia), respectively. The Microtox® reagents were supplied from Modern Water Inc. (USA).

2.2. Electrochemical oxidation of ACE-K

The electrolytic experiments were conducted in a divided and thermostated cell at the constant current density of 0.1 A/cm^2 and 25 °C temperature. The anode and cathode compartments were separated by a Nafion 212 cation-exchange membrane separator. The anolyte (100 mL) was 1 M Na_2SO_4 containing ACE-K, while the catholyte (100 mL) was 1 M Na_2SO_4 only. A commercial BDD electrode (CONDIAS GmbH, Germany) was used as the anode while a stainless steel plate (SS 304) was used as the cathode. Both electrodes had the same geometric working surface areas (2 cm^2). A DC power supply (Good Will Instrument Co. Ltd. GPS-2303) was employed to perform the experiments. Samples were taken at intervals during electrolysis. All experiments were performed in triplicate.

2.3. Analytical methods

The real environmental water samples were collected in southern Taiwan. The analytic methods and instruments used for measuring water quality parameters were stated elsewhere [8]. A high performance liquid chromatography (HPLC) instrument (Hitachi Chromaster 5420) was employed to analyze the concentrations of ACE-K and organic acids of electrolysis samples.

The compound separations in HPLC analysis were carried out in ambient temperature by a Chromolith SpeedROD RP-18 endcapped column (100 × 4.6 mm I.D.). The mobile phase consisted of solvents A (acetonitrile) and B (0.01 M phosphate buffer (pH = 5.0)) was operated at flow rate = 4 mL/min. The gradient was performed at the mobile phase of 3A:97B (v/v) within a period of 3 min. For the organic acid analysis, a 300 mm BIO-RAD aminex HPX-87H ion exclusion column was used to separate compounds at 35 °C. The mobile phase was 100% 4 mM H_2SO_4 operated at 0.6 4 mL/min within 30 min analysis. The working wavelengths of ACE-K and organic acid analysis were 227 and 210 nm, respectively.

The degradation intermediates of ACE-K were analyzed using a Thermo LCQ Deca XP system LC-MS, and the chromatographic separation was performed on a Phenomenex C18 100A column (150 × 2.1 mm I.D., 5 µm, Kinetex). The mobile phases were 20 mM ammonium acetate in distilled deionized water (mobile phase A) and 20 mM ammonium acetate in methanol (mobile phase B). The gradient elution program was set as follows: mobile phase B, 2–75% (0–13 min), 75% (13–17 min), 75–2% (17–18 min), and 2% (18–30 min). The flow rate was set as 0.2 mL/min. The scan range was 50–250 (*m/z*) in negative mode. Inorganic ions generated during electrochemical oxidation process were detected using DIONEX ICS-3000 ion chromatography. A Hitachi F-7000 fluorescence spectrometer was used to obtain the excitation-emission matrix (EEM) spectra. Prior to the fluorescence EEM analysis, all samples were adjusted to pH = 2.0 using sulfuric acid. The UV–vis absorbance and UV_{254} were measured by a Hitachi U-2900 UV–vis spectrophotometer equipped with a 1 cm path length quartz cell. The SUVA values of samples can be calculated by Eq. (1) [11].

$$\mathrm{SUVA(L/mg-M)} = [\mathrm{UVA(1/cm)/DOC(mg/L)}] \times 100\mathrm{cm/M} \quad (1)$$

The UVA is calculated from UVA = A/d equation, where A is the measured UV absorbance at 254 nm for the sample filtered through a 0.45 μm filter, and d is the quartz cell path length in cm. The dissolved organic carbon (DOC) of each sample was measured using a Shimadzu (TOC-5000) or Teledyne Tekmar (Model No. 15-0030-200) TOC analyzer. Before the measurement, each sample was also filtered through a 0.45 μm filter. The toxicity responses of electrolyzed matrices were tested using a Modern Water Microtox® Model 500 Analyzer. The luminescence inhibition percentage values were calculated after 5 and 15 min exposures of samples to *Vibrio fischeri* bacteria. Statistical analysis was performed using the IBM SPSS Advanced Statistics 24.

3. Results and discussion

3.1. Electro-degradation of ACE-K on BDD and degradation intermediates

It is common that the concentration of target compound used in degradation intermediate measurement is much higher than that used in degradation kinetics test so that the intermediates can be easily obtained and detected, although the kinetics of target compound destruction and intermediate formation is usually lower at a significantly greater initial concentration (C_0). Therefore, the C_0 values of ACE-K used in Sections 3.1 and 3.2 (degradation intermediate measurement) and 3.3 (degradation kinetics

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