Degradation of acesulfame in aqueous solutions by electro-oxidation

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ABSTRACT

The electrochemical oxidation of acesulfame (acesulfame potassium (ACE-K)) on different electrodes or in various aqueous solutions was investigated in this study. The performance in terms of ACE-K degradation and total organic carbon (TOC) removal of tested anodes was in the order boron-doped diamond (BDD) > PbO_2 > Pt, although ACE-K could not be directly oxidized on these electrodes in cyclic voltammetric analysis. At the same electrolysis time, the ACE-K degradation and TOC removal efficiencies increased with an increasing current density or anode area, but decreased with the increase of initial ACE-K concentration. The ACE-K degradation was slightly influenced by temperature at $25-50\,°C$. The apparent pseudo-first-order rate constants of ACE-K oxidation were similar in ACE-K-spiked 1 M Na_2SO_4 solution and municipal wastewater matrices (influent (IN), before biological treatment (BBT), and after biological treatment (ABT)) ($(1.73 - 2.32) \times 10^{-3}$ s^{-1}). Although the TOC removal (consistent with mineralization current efficiency) in these wastewater matrices followed the order ABT ≈ IN > BBT, the complete mineralization of ACE-K and TOC was achieved. Accordingly, the electrooxidation process has great potential to be used to improve the biodegradation-resistant ACE-K degradation and TOC removal in secondary biological wastewater treatment.

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1. Introduction

Acesulfame is a calorie-free sugar substitute which is 200 times sweeter than sugar, so it is widely used in foods and beverages around the world [1]. The wide use of artificial sweeteners has drawn attention to environmental concerns recently. Especially, acesulfame (one of artificial sweeteners) has been found in high concentration as an emerging contaminant in wastewater, groundwater, surface water, and drinking water systems [2–6]. With a frequency of detection of 93%, acesulfame was one of the emerging polar organic contaminants with the highest median concentration levels in European WWTPs (the highest concentration = 2.5 mg/L). The typical entrance pathway of acesulfame into aquatic environment is *via* municipal wastewaters [7,8], and it is persistent in surface and coastal waters [9]. Although the concentrations of acesulfame and other artificial sweeteners are in the levels of micrograms to miligrams per liter in aquatic environment, there is a huge safety margin of acesulfame regarding its potential adverse health effects to human [6]. Therefore, it is important to remove acesulfame or decompose it into innocuous species in wastewater treatment.

However, conventional activated sludge processes cannot remove or eliminate acesulfame because it is not biodegraded in aerobic biologically active treatment [7]. Various studies have reported the frequent detection of acesulfame in wastewater treatment plant (WWTP) effluents [6,9]. Therefore, acesulfame is suitable to be used as a wastewater tracer under aerobic conditions [7] or a persistent anthropogenic wastewater indicator [8]. Poor removal for acesulfame was observed in conventional multi-barrier drinking water treatment [7]. Acesulfame was found to be photodegradable [10], while the degradation of acesulfame was very slow in some advanced oxidation processes (AOPs) such as O_3/H_2O_2, $O_3/UV-C$, $H_2O_2/UV-C$, sonolysis, or the irradiation of water *via* electron beams or gamma rays [11].

Electrochemical oxidation is also an AOP method which has been increasingly used for environment contaminant destruction in recent years. Boron-doped diamond (BDD) anodes, with more positive oxygen evolution potentials than dimensionally stable anodes (DSA) (*e.g.*, Ti/IrO_2, Ti/SnO_2, and Ti/PbO_2), are more stable and better than Pt and DSA for highly efficient electrochemical oxidation of organic pollutants [12–16]. However, little is known for the degradation of acesulfame by electrochemical oxidation. Accordingly, in this study a BDD electrode was used to explore the electrochemical behavior and the electro-degradation of acesulfame in aqueous media. For comparison, a commercial Pt electrode and a lab-prepared PbO_2/Ti plate were also tested. The effects of

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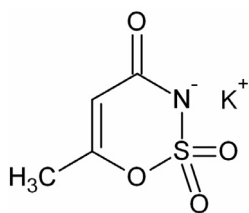
Fig. 1. Chemical structure of ACE-K.

current density, anode area, temperature, initial concentration, and municipal (or domestic) wastewater matrix on acesulfame electro-degradation were studied. The data obtained from this study are useful and practical to be used for the electrochemical degradation of acesulfame in real municipal wastewater matrices.

2. Materials and methods

2.1. Chemicals

Acesulfame potassium (ACE-K, $C_4H_4KNO_4S$ (Fig. 1)) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). All ACE-K solutions were prepared by dissolving ACE-K in background electrolyte. Acetonitrile (HPLC grade solvent) and phosphoric acid (65%) were obtained from ECHO Chemical Co. Ltd. (Taiwan) and Scharlau (Spain), respectively. Sodium sulfate and trisodium phosphate 12-water were supplied from SHOWA Co. Ltd. (Japan).

2.2. Cyclic voltammetry (CV) of ACE-K

Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of the ACE-K in prepared solutions. All CV measurements were conducted using a CHI 660B electrochemical workstation (CH Instruments, Inc., USA) which was connected to a personal computer. A commercial BDD (CONDIAS GmbH, Germany), Pt (Spemet Co. Ltd., Taiwan) or lab-prepared PbO_2 electrode was used as the working electrode. All tested anodes had the same geometric working surface areas which are $2\,cm^2$. The PbO_2 electrode was prepared using the method described elsewhere [17]. The counter electrode was a platinum wire, whereas the reference electrode was Ag/AgCl (3 mol KCl dm^{-3}, 0.207 V *vs* SHE (standard hydrogen electrode) at 25 °C). Sodium sulfate solutions are commonly used for the electro-degradation tests of aqueous (emerging) organic pollutants. In this study, 1 M Na_2SO_4 was used as the supporting electrolyte to enhance the conductivity of tested solutions and to lower the cell voltage of (H-type) electrolytic cell. The stock solution of ACE-K (100 mg/L) was prepared by dissolving ACE-K into 1 M Na_2SO_4. The potential scan (100 mV/s) of CV was conducted over the range of −0.7–2.5 V (*vs* Ag/AgCl).

2.3. Electrochemical oxidation of ACE-K

Electrolysis experiments were carried out in a divided and thermostated cell. The anolyte (100 mL) was 1 M Na_2SO_4 containing ACE-K, while the catholyte (100 mL) was only 1 M Na_2SO_4. The anode and cathode compartments were separated by a Nafion 212 cation-exchange membrane separator. Prior to use, the Nafion 212 was heated at 65 °C in 1 M (~3%) H_2O_2 for 1 h to remove organic impurities. The membranes were washed 3 times with deionized distilled water (DDW) and stored in DDW. A BDD, Pt, or PbO_2 electrode was employed as the anode while a stainless steel plate (SS 304) was used as the cathode. All the experiments were performed using a DC power supply (Good Will Instrument Co. Ltd. GPS-2303). The cell voltage and current were monitored with time

by reading the data on DC power supply. Solutions in each compartment were well stirred using a magnetic stirrer. The solution pH and temperature were measured.

The domestic wastewater samples were collected in southern Taiwan. The total organic carbon (TOC) was analyzed using a Shimadzu TOC-5000 analyzer. The biological oxygen demand (BOD) analysis was conducted in a BOD incubator (Incubator 721, HJHT). The chemical oxygen demand (COD) was analyzed by a COD analyzer (COD Reactor CR25, Rocker) coupled with a colorimeter (Hach-DR-890). A Lutron DO-5510 instrument and a Shimadzu UV-1601 analyzer were used to measure dissolved oxygen (DO) and PO_4^{3-}, respectively. The analysis of dissolved solids (DS) was performed using the Method 2540 in the Standard Methods [18]. The pH, conductivity and oxidation–reduction potential (ORP) were measured by a TS-100 pH meter, an SC-170 conductivity meter, and an SP-2200 microprocessor pH Meter (Suntex, Taiwan), respectively.

2.4. Analytical methods

Samples were taken at intervals during 120 min of the electrolysis. The concentrations of residual ACE-K were analyzed by a high performance liquid chromatography (HPLC) instrument (Hitachi Chromaster 5420). The separations were carried out in ambient temperature by a Chromolith SpeedROD RP-18 endcapped column 50 × 4.6 mm. The mobile phase consisted of solvents A (acetonitrile) and B (0.01 M Phosphate buffer pH 5.0) operated with a flow rate of 4 mL min^{-1}. The gradient was performed at the mobile phase of 3A:97B (v/v) within a period of 3 min analysis. The injection volume was 20 μL and the working wavelength was 227 nm. After the TOC concentrations in samples were analyzed, the mineralization current efficiency (MCE) of electrolyzed ACE-K solutions at a given time t (h) was calculated by Eq. 1 [19].

$$MCE(\%) = \frac{nFV_s\Delta(TOC)_{exp}}{4.32 \times 10^7 mIt} \times 100 \qquad (1)$$

where F is the Faraday constant (96,487 C/mol), V_s is the volume of solution (L), $\Delta(TOC)_{exp}$ is the experimental TOC removal (mg/L), 4.32×10^7 is a conversion factor (3600 s/h × 12,000 mg C/mol), m is the number of carbon atoms (4 atoms) in a ACE-K molecule, and I is the applied current (A). The number of electrons consumed in the mineralization process (n) was set as 24, assuming that the overall mineralization of the ACE-K follows Reaction 2:

$$C_4H_4KNO_4S + 8H_2O \rightarrow 4CO_2 + NH_4^+ + K^+ + SO_4^{2-} + 16H^+ + 16e^-$$
$$(2)$$
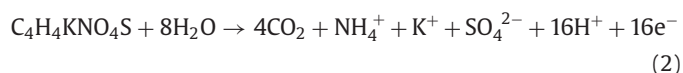
3. Results and discussion

3.1. Effect of anode material on ACE-K degradation

3.1.1. Cyclic voltammetric analysis of ACE-K on different electrodes

The electrochemical behavior of ACE-K at Pt, PbO_2 and BDD in 1 M Na_2SO_4 (background electrolyte) were examined by cyclic voltammetric (CV) experiments. Fig. 2a shows the cyclic voltammograms of ACE-K on Pt in background electrolyte compared to background electrolyte. The cyclic voltammograms of 1 M Na_2SO_4 in the presence and absence of ACE-K were nearly overlapped, so no signal of ACE-K oxidation was detected in the CV scanning window (between hydrogen and oxygen evolution), indicating that ACE-K could not be directly oxidized on Pt. The reduction peak at 0.22 V *vs* Ag/AgCl was due to the reduction of platinum oxide, whereas that at −0.19 V *vs* Ag/AgCl should be resulted from hydrogen adsorption. Likewise, the CV analysis also reveals that ACE-K could not be directly oxidized on PbO_2 (Fig. 2b). The oxidation peaks at