Removal of artificial sweetener aspartame from aqueous media by electrochemical advanced oxidation processes

Heng Lin [a, b], Nihal Oturan [b], Jie Wu [b, c], Virender K. Sharma [d], Hui Zhang [a, **],
Mehmet A. Oturan [b, *]

[a] Department of Environmental Engineering, Wuhan University, Wuhan 430079, China
[b] Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454, Marne-la-Vallée, France
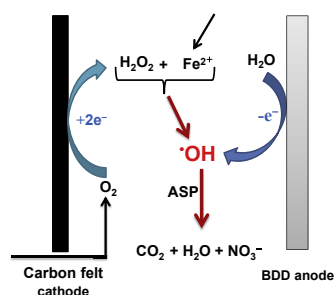[c] Fuzhou Environmental Monitoring Center, Fuzhou 350011, China
[d] Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, College Station, TX, 77843, USA

HIGHLIGHTS

- Effective removal of aspartame (ASP) by electro-Fenton process.
- Effect of current and catalyst concentration on mineralization rate of ASP.
- Determination of rate constant for oxidation of ASP by •OH as $5.23 \times 10^9 \ M^{-1} \ s^{-1}$.
- Nitrogen present in ASP is released as oxamic acid and nitrate/ammonium ions.
- Toxicity assessment by Microtox highlights detoxification of treated solution.

GRAPHICAL ABSTRACT

ABSTRACT

The degradation and mineralization of aspartame (ASP) in aqueous solution were investigated, for the first time, by electrochemical advanced oxidation processes (EAOPs) in which hydroxyl radicals were formed concomitantly in the bulk from Fenton reaction via in situ electrogenerated Fenton's reagent and at the anode surface from the water oxidation. Experiments were performed in an undivided cylindrical glass cell with a carbon-felt cathode and a Pt or boron-doped diamond (BDD) anode. The effect of Fe^{2+} concentration and applied current on the degradation and mineralization kinetics of ASP was evaluated. The absolute rate constant for the reaction between ASP and •OH was determined as $(5.23 \pm 0.02) \times 10^9 \ M^{-1} \ s^{-1}$ by using the competition kinetic method. Almost complete mineralization of ASP was achieved with BDD anode at 200 mA constant current electrolysis. The formation and generation of the formed carboxylic acids (as ultimate end products before complete mineralization) and released inorganic ion were monitored by ion-exclusion high performance liquid chromatography (HPLC) and ion chromatography techniques, respectively. The global toxicity of the treated ASP solution during treatment was assessed by the Microtox® method using V. fischeri bacteria luminescence inhibition.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Artificial sweeteners, the ingredients of dietary products, are consumed considerably in food, beverages, drugs and sanitary

* Corresponding author.
** Corresponding author.
E-mail addresses: eeng@whu.edu.cn (H. Zhang), Mehmet.oturan@univ-paris-est.fr (M.A. Oturan).

products (Kroger et al., 2006; Buerge et al., 2010; Lange et al., 2012). As a kind of emerging contaminants, artificial sweeteners are considered in environmental sciences recently (Giger, 2009). The studies on occurrence, fate, and ecotoxicological effects of artificial sweeteners in aquatic environment have been increasing rapidly since 2009 (Lange et al., 2012; Sharma et al., 2014). Several studies have reported adverse human health effects of the application of artificial sweeteners (Lange et al., 2012; Toth et al., 2012). The long-term health effects, resulting from the chronic exposure to low levels of these compounds, are largely unknown (Mawhinney et al., 2011).

Some of the artificial sweeteners are difficult to degrade by conventional wastewater treatment processes (Bernardo et al., 2006). Consequently, advanced oxidation processes (AOPs) have been proposed as an alternative method to degrade artificial sweeteners effectively (Sharma et al., 2014). AOPs involve the "in-situ" generation of strong oxidants, especially hydroxyl radicals (•OH), which are highly reactive species ($E^0 = 2.80$ V/SHE) (Brillas et al., 2009; Lin et al., 2014; Oturan and Aaron, 2014; Brillas and Martínez-Huitle, 2015; Martínez-Huitle et al., 2015). These radicals lead to the oxidative degradation of organic pollutants by electron transfer, hydrogen atom abstraction reaction or electrophilic addition to π systems (Brillas et al., 2009; Özcan et al., 2013; Vasudevan and Oturan, 2014). These radicals are able to oxidize organics until ultimate oxidation degree, i.e., their transformation to CO_2 (Oturan, 2014; Rodrigo et al., 2014).
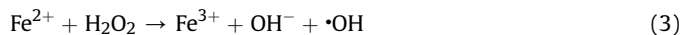
Different AOPs have been applied to remove artificial sweeteners from water (Keen and Linden, 2013; Sharma et al., 2014). For example, Soh et al. (2011) degraded 1 μM artificial sweeteners by applying 100 μM ozone; acesulfame-K was not detected at 5 min while 6% sucralose remained after 60 min. Sucralose and acesulfame-K were also treated using UV irradiation procedure (Soh et al., 2011). The results showed that sucralose did not degrade after 5 h UV exposure and acesulfame-K was found to be removed by about 35%. In addition, Keen and Linden (2013) removed 0.500 mg L^{-1} sucralose by UV/H_2O_2 processes and found that sucralose degradation was efficient at high irradiation intensity, i.e., 4000 mJ cm^{-2}. In contrast, Sharma et al. (2012) found that sucralose can be efficiently oxidized by ferrate(VI). More recently, Lin et al. (2016) investigated the efficient mineralization of saccharin in water by electrochemical AOPs; demonstrating this molecule can be effectively destroyed by AOPs.

Among various AOPs, electrochemical advanced oxidation processes (EAOPs) have attracted much more attention in recent years because of their low operating cost and environmental compatibility (Brillas et al., 2009; Oturan et al., 2013, 2015). Based on in situ generation of hydroxyl radicals, there are two kinds of commonly used EAOPs: electrochemical oxidation (EO) and electro-Fenton (EF) processes (Oturan and Aaron, 2014; Sirés et al., 2014). In EO processes, organic pollutants are destroyed by electro-generated heterogeneous hydroxyl radicals M(•OH) on high oxygen overvoltage anodes (M) according to Eq. (1) (Marselli et al., 2003; Panizza and Cerisola, 2009; Wu et al., 2012; Nidheesh and Gandhimathi, 2014; Martínez-Huitle et al., 2015).

$$M + H_2O \rightarrow M(•OH) + H^+ + e^- \qquad (1)$$

In contrast, EF process involves the continuous generation of H_2O_2 from the two-electron reduction of dissolved O_2 in the reaction medium (Eq. (2)) when using a carbonaceous cathode, e.g., carbon felt (Lahkimi et al., 2007), carbon-PTFE air-diffusion electrode (Garcia-Segura and Brillas, 2011), carbon sponge (Özcan et al., 2008b) and graphite (Nidheesh et al., 2014). Recently BDD anode was also used in H_2O_2 generation (García et al., 2014). The in situ formed H_2O_2, reacts with externally added Fe^{2+} ions in a catalytic

amount to generate homogeneous hydroxyl radicals (•OH) following the well-known Fenton's reaction (Eq. (3)). Fe^{2+} consumed in the Fenton reaction is then regenerated electrochemically according to Eq. (4) to catalyze the formation of •OH via Fenton's reaction (Brillas et al., 2009; Mousset et al., 2016).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + •OH \qquad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$

Notably, in the case of a high O_2-overvoltage anode use (e.g. BDD in electro-Fenton process) the efficiency of the process is enhanced due to high amount of hydroxyl radical concomitantly production from equations (1) and (3) (Oturan and Aaron, 2014).

As the "first generation" sweeteners (Berset and Ochsenbein, 2012), aspartame (ASP) is a white dipeptide, crystalline, low-caloric sweetener, which is 180–200 times sweeter than sucrose (Conceição et al., 2005). ASP was found in all of the surface waters at a concentration up to 0.21 mg/L in Tianjin, China (Gan et al., 2013). ASP has been found not to be stable in solution under light irradiation (Kim et al., 1997) and can decompose at under normal usage conditions (Sang et al., 2014). The risks of ASP ingestion would be in the toxicity of its metabolism products. One of its metabolites is methanol which may cause acidoses and blindness (Conceição et al., 2005).

To the best of our knowledge, degradation of aspartame in aqueous solution has not been studied by either AOPs or by EAOPs. Therefore, in this study, we have following aims: (i) study the oxidative degradation of ASP in acidic aqueous solution by using EF process in order to investigate oxidation and mineralization behavior of the ASP against hydroxyl radicals, (ii) investigate the kinetics of oxidative degradation of ASP by •OH/M(•OH) during EF process, (iii) determine the absolute rate constant of the reaction between ASP and •OH using the competition kinetic method (Özcan et al., 2009; Bocos et al., 2016), (iv) examine the effect of the applied current and Fe^{2+} concentration on the oxidative degradation of ASP and mineralization of its aqueous solution, (v) evaluate the formation and evolution of aliphatic short-chain carboxylic acids, formed as end-products before complete mineralization, and the concentration of inorganic ions released into the solution, and (vi) finally, assess the toxicity of initial ASP solution and its evolution throughout the treatment by the Microtox method.

2. Materials and methods

2.1. Chemicals

ASP, N-L-α-aspartyl-L-phenylalanine methyl ester ($C_{14}H_{18}N_2O_5$, ≥98% purity), was obtained from Alfa Aesar and was used in the electrolytic experiments without purification. The chemical structure and main characteristics of ASP are presented in Table SM-1. Anhydrous sodium sulfate (analytical grade) was obtained from Sigma-Aldrich. Ferrous sulfate heptahydrated of analytical grade as a catalyst source was purchased from Acros Organics. Analytical grade benzoic acid (BA) of reagent grade was acquired from Sigma-Aldrich and was used as the competition substrate in several kinetic experiments. Analytical grade carboxylic acids and other chemicals used in chromatographic analysis were purchased from Acros, Sigma, Riedel-de Haën and Fluka. All solutions were prepared with ultrapure water, which was obtained from a Millipore Mill-Q system with resistivity >18 MΩ cm at room temperature.