



Elimination of radiocontrast agent Diatrizoic acid from water by electrochemical advanced oxidation: Kinetics study, mechanism and mineralization pathway



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ABSTRACT

Diatrizoic acid (DIA) is an iodinated X-ray contrast media commonly used in hospitals. It is persistent and recalcitrant in aquatic environments and difficult to biodegrade. Thus, we studied its removal from aquatic medium by two electrochemical advanced oxidation processes: anodic oxidation and electro-Fenton using BDD anode and carbon felt cathode. The effect of two of the most important variables on, i.e., applied current intensity (both processes) and catalyst concentration (electro-Fenton) was assessed to optimize oxidative degradation of DIA and mineralization rate of its aqueous solution. 1000 mA current intensity and 0.2 mM catalyst (Fe^{2+}) concentration (at pH 3) were determined as optimal operating values for its effective removal from water based on the following parameters: concentration decay of DIA, total organic carbon removal rate and mineralization current efficiency. The rate constant for oxidation of DIA by $\cdot\text{OH}$ was determined using competition kinetics method and found be $3.96 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. Obtained results showed a quick and complete mineralization of DIA solution. In addition, the identification of aromatic intermediates, short-chain carboxylic acids and mineral ions released to the solution during electro-Fenton treatment allowed us proposing a plausible mineralization mechanism of DIA by $\cdot\text{OH}$ generated in the process. Finally, the toxicity of treated solutions along time was assessed following the luminescence inhibition of the marine bacteria *Vibrio fischeri*, using Microtox® method.

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1. Introduction

During the last two decades, a vast number of micro pollutants have been found in the aquatic environment. Arising from many sources such as industrial, agriculture, and urban activities, most of them are among organic persistent pollutants (POPs) and are highly toxic for living organisms [1]. Among the POPs, pharmaceutical products and their metabolites have been detected in the different water sources at concentrations of ng L^{-1} to $\mu\text{g L}^{-1}$ [2–5]. Even at low concentration, their continuous releases constitutes an enormous potential risk for living beings, given their high persistence and toxic potential due to synergistic effects [6]. Given the increasing scarcity of the water resources and the growing demand of this source, the prime concern of scientific community is to develop environment friendly and cost effective technologies able to overcome the problem of treatment of wastewater contaminated by hazardous pollutants before their introduction to the natural water stream. As the conventional wastewater treatment plants (WWTPs) are not designed for removal of POPs, pharmaceutical products and their metabolites usually pass through such facilities without an effective depletion of their concentration. Therefore development

of effective and affordable wastewater treatments techniques becomes primordial to destroy the POPs and to prevent their injection in the environment in order to preserve natural water resources.

Iodinated contrast media (ICM) is one of the most extensively dosed pharmaceuticals in hospitals by intravascular administration. Among them, DIA is used as X-ray contrast media since the 1950s. This drug is generally applied in elevated dosages and excreted almost non-metabolized due to its hydrophilic character and structural design [7,8], reason why it has been founded in WWTPs inflows at concentrations up to $100 \mu\text{g L}^{-1}$ [9,10]. It can be degraded to stable by-products more harmful than the mother molecule in the food chain. Besides, these by-products constitute the main responsible of the presence of adsorbable organic halogen (AOX) in the inflows of hospital effluents, with the potential toxic effect for human health [11]. Although its negative effect in human health after continuous exposure is still unknown [12], in response to concerns about the presence of DIA in water, different processes have been assessed for the treatment of this drug and its metabolites [12–15] over the past years. However, some of them have demonstrated to be unable to achieve its total mineralization. Among different methods applied to the treatment of wastewaters, advanced oxidative processes (AOPs) have demonstrated their high effectiveness on the mineralization and degradation of pharmaceuticals from water [16–19]. AOPs involve the in situ generation of strong oxidants, mainly

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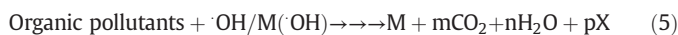
hydroxyl radical ($\cdot\text{OH}$), a non-selective and highly strong oxidizing agent, able to destroy efficiently the POPs [20,21]. Among them, electrochemical advanced oxidative processes (EAOPs) have emerged during the last years as promising alternatives for wastewater treatment [22, 23]. They include electrochemical processes to generate the proper reagents to support Fenton's reaction [23] or produce directly $\cdot\text{OH}$ on the surface of an appropriate anode [24]. The generation of these reagents is strongly conditioned by the cell potential, solution conditions and the nature of the electrodes [25]. One of the well-known EAOPs is the anodic oxidation (AO) process in which organic pollutants can be oxidized by direct electron transfer to the anode or by generation of $\cdot\text{OH}$ occurred as a consequence of the electrochemical discharge of water on an adequate anode (Eq. (1)). Depending on the nature of anode material (M) the $\cdot\text{OH}$ formed can interact more or less strongly with anode surface (chemisorption or physisorption) influencing their availability to oxidize organic compounds [26–29].



Actually, electro-Fenton (EF) process is one of the most popular EAOPs [22,23]. It is based on the electrocatalytic in situ formation of $\cdot\text{OH}$ via Fenton reaction (Eq. (2)) in which H_2O_2 is generated by 2-electron reduction of dissolved O_2 (Eq. (3)) and ferrous iron that acts as homogeneous catalyst is regenerated from Fe^{3+} formed by Fenton reaction [30–33].



The homogeneous ($\cdot\text{OH}$) and heterogeneous ($\text{M}(\cdot\text{OH})$) radicals thus formed are powerful oxidants able to degrade recalcitrant pollutants and their intermediates in aqueous medium following Eq (5) until mineralization [22,23,26], i.e., their conversion to CO_2 , water and inorganic ions.



There is a lack of report on elimination of DIA in the literature. There are very few publications on its degradation by photocatalysis [34,35] or adsorption on activated carbon [36]; however to the best of our knowledge, the removal of DIA from water has not been already studied by electrochemical advanced technology. Therefore in this work, we describe an effective removal of this harmful pollutant from water/wastewater by using EAOPs in an undivided electrochemical cell equipped with a BDD anode and a carbon-felt cathode. The effect of the catalyst dosage and applied current intensity on oxidative degradation of DIA and mineralization rate of its aqueous solution was investigated. In order to attain a better understanding of the mineralization process occurred during the treatment, aromatic/cyclic organic intermediates formed during the treatment, the formation and evolution of short-chain carboxylic acids, as well as the inorganic ions released during the treatment were monitored by GC–MS, HPLC, ion chromatography, respectively. Finally, based on results obtained and literature findings it was possible to propose a plausible reaction pathway for the mineralization of DIA by $\cdot\text{OH}/\text{M}(\cdot\text{OH})$ produced in EF process with BDD anode.

2. Material and methods

2.1. Chemicals

The pharmaceutical Diatrizoic acid ($\text{C}_{11}\text{H}_9\text{I}_3\text{N}_2\text{O}_4$) and sodium sulfate (supporting electrolyte) were supplied by Sigma Aldrich. Sulfuric acid (ACS reagent grade, 98%); iron (II) sulfate heptahydrate (used as

catalyst source, 99%) and methanol (HPLC analysis grade) were purchased from Acros Organics in analytical grade. 0.1 mM DIA solutions were prepared with ultrapure water obtained from a Millipore Milli-Q Simplicity 185 system with resistivity $> 18 \text{ M}\Omega \text{ cm}$ at 25°C . The pH of solutions was adjusted using analytical grade sulfuric acid or sodium hydroxide (Acros).

2.2. Electrochemical cell and apparatus

The experiments were performed in an open and undivided cylindrical glass cell with a volume capacity of 250 mL at room temperature. A 3D carbon felt ($18.0 \text{ cm} \times 5.0 \text{ cm} \times 0.5 \text{ cm}$, from Mersen, France) was used as cathode. It was placed on the inner wall of the cell, covering the total internal perimeter. The anode was a 25-cm^2 BDD film on niobium support (from CONDIAS GmbH, Germany), centered in the electrolytic cell. Na_2SO_4 (0.05 M) was added to the cell as background electrolyte. Prior to electrolysis, compressed air at about 1 L min^{-1} was bubbled during 5 min through the solution to ensure O_2 saturation, thus ensuring the H_2O_2 production from reduction of dissolved O_2 . Besides, the solution was continuously agitated by a magnetic stirrer (250 rpm) to get mass transfer to/from electrodes. The pH of the solutions was adjusted to 3.0 by using 1.0 M H_2SO_4 and was measured with a CyberScan pH 1500 pH meter from Eutech Instruments. For the electro-Fenton experiments, an adequate concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to initial solutions as source of Fe^{2+} as catalyst. A range of currents from 100 to 1000 mA was applied to the electrochemical cell to carry out the degradation and mineralization kinetics. The current and the amount of charge passed through the solution were measured and displayed continuously throughout electrolysis by using a DC power supply (HAMEG Instruments, HM 8040-3).

2.3. Analytical measurements

The determination of decay kinetics of DIA was monitored by HPLC using a Merck Lachrom Liquid chromatography equipped with an L-2310 pump, fitted with a reverse phase column Pursopher RP-18, $5 \mu\text{m}$, $25 \text{ cm} \times 4.6 \text{ mm}$ (i.d.) column and coupled with an L-7455 photodiode array detector. The temperature of the column was maintained constant at 40°C . The UV Spectrum of DIA was measured setting the detector at $\lambda = 238 \text{ nm}$ (maximum absorption wavelength). The injection volume was set at $20 \mu\text{L}$ and the isocratic eluent 30:70 methanol/water (0.1% phosphoric acid) (v/v) was pumped to the system at a flow rate of 0.7 mL min^{-1} .

Generated aliphatic carboxylic acids were quantified by ion-exclusion HPLC using an Alltech chromatograph equipped with a Model 426 pump, fitted with a Supelcogel H, $9 \mu\text{m}$, $25 \text{ cm} \times 4.6 \text{ mm}$ (i.d.), column at room temperature, and coupled with a Dionex AD20 UV detector selected at $\lambda = 220 \text{ nm}$. A 0.1% H_3PO_4 solution at a flow rate of 0.5 mL min^{-1} was used as the mobile phase. The measurements were controlled through Chromeleon SE software and the identification of intermediates was made by comparison of retention time and UV spectra with those of pure standards.

Nitrate and iodine ions released to the treated solutions during treatment were analysed using a Dionex ICS-1000 Basic Ion Chromatography system equipped with a DS56 conductivity detector containing a cell heated at 35°C under control through Chromeleon SE software, using an IonPac AS4A-SC, $25 \text{ cm} \times 4 \text{ mm}$ (i.d.), anion-exchange column, linked to an IonPac AG4A-SC, $5 \text{ cm} \times 4 \text{ mm}$ (i.d.), column guard. The mobile phase was a mixture of 1.7 mM sodium bicarbonate and 1.8 mM sodium carbonate circulating at 2.0 mL min^{-1} . The sensitivity of the detector was improved using an ASRS-ULTRA II self-regenerating suppressor. Ammonium ion was analysed using the same IC with an IonPac CS12A, $25 \text{ cm} \times 4 \text{ mm}$ (i.d.), cation-exchange column, linked to an IonPac CG12A, $5 \text{ cm} \times 4 \text{ mm}$ (i.d.), column guard. The CRS-ULTRA II self-regenerating suppressor was used. The mobile phase was a solution of 9.0 mM sulfuric acid circulating at 1.0 mL min^{-1} .

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