Iodinated contrast media electro-degradation: Process performance and degradation pathways

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HIGHLIGHTS

- The electrochemical degradation of six iodinated contrast media were investigated.
- Treatment feasibility as well as reaction by-products and toxicity were investigated.
- In all the investigated cases, the removal efficiency was higher than 80%.
- Two main degradation pathways were identified.

ARTICLE INFO

ABSTRACT

The electrochemical degradation of six of the most widely used iodinated contrast media was investigated. Batch experiments were performed under constant current conditions using two DSA® electrodes (titanium coated with a proprietary and patented mixed metal oxide solution of precious metals such as iridium, ruthenium, platinum, rhodium and tantalum). The degradation removal never fell below 85% (at a current density of 64 mA/cm^2 with a reaction time of 150 min) when perchlorate was used as the supporting electrolyte; however, when sulphate was used, the degradation performance was above 80% (at a current density of 64 mA/cm^2 with a reaction time of 150 min) for all of the compounds studied. Three main degradation pathways were identified, namely, the reductive de-iodination of the aromatic ring, the reduction of alkyl aromatic amides to simple amides and the de-acylation of N-aromatic amides to produce aromatic amines. However, as amidotrizoate is an aromatic carboxylate, this is added via the decarboxylation reaction. The investigation did not reveal toxicity except for the lower current density used, which has shown a modest toxicity, most likely for some reaction intermediates that are not further degraded. In order to obtain total removal of the contrast media, it was necessary to employ a current intensity between 118 and 182 mA/cm^2 with energy consumption higher than 370 kWh/m^3. Overall, the electrochemical degradation was revealed to be a reliable process for the treatment of iodinated contrast media that can be found in contaminated waters such as hospital wastewater or pharmaceutical waste-contaminated streams.

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1. Introduction

Iodinated contrast media (ICM) are used for imaging soft tissues, internal organs and blood vessels and can be given to humans at doses of up to 200 g per diagnostic session (Weissbrodt et al., 2009). In medical diagnostics, ICM are applied in high amounts, accounting for over 3.5×10^6 kg per year worldwide (Pérez and Barceló, 2007). As they are composed of a benzene ring and three atoms of iodine, these compounds are the best combination of stability and high x-ray absorption, together with low toxicity, even when decomposed. The elimination of the contrast material from the body involves the reduction of the concentration of the blood with plasma. In extravascular regions, contrast agent returns to the plasma. This phase lasts for a few hours until all of the

ICM has been ultra-filtered by the kidney (Verburg et al., 2013). While in some countries (e.g., Japan, China, Greece) wastewater from large hospitals is pre-treated or biologically treated on site, in many other countries, it is directly connected to a municipal sewer and treated at municipal wastewater treatment plants (Pauwels and Verstraete, 2006). Owing to their high persistence, ICM pass through conventional wastewater treatment systems (Kümmerer, 2001; Putschew et al., 2000). Accordingly, ICM are commonly detected at quite elevated concentrations in wastewaters, surface waters, groundwater, bank infiltrate and soil leachates because of their high polarity and persistence (Kormos et al., 2010). Trace amounts of ICM have even been found in drinking waters been produced directly from surface water (Seitz et al., 2006). It is not surprising, therefore, that the concentration of pharmaceuticals in effluents and surface waters are in the μg/L range (Anquandah et al., 2011). Moreover, Forrez et al. (2011) have found secondary effluent ICM concentrations in the range of mg/L. Also, little is

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known about the occurrence and fate of these drug metabolites. In general, it is likely that metabolites will be less biologically active than their parent drugs (Carballa et al., 2004; Drewes et al., 2001; Pérez and Barceló, 2007; Nita and Soltis, 2011). However, metabolites could be cleaved by bacteria that are present in wastewater treatment plants or rivers, hence regenerating the active parent pharmaceutical (Touraud et al., 2011). Busetti et al. (2010) placed particular emphasis on environmental risk due to concentrations of ICM in the water matrix. The presence of pharmaceutical compounds in the environment has led to growing concern because relatively little is known about their impact on the health of humans and ecosystems, especially concerning chronic toxicity from continuous exposure to multiple compounds at doses far below medicinal ones (Jeong et al., 2010). The elimination of ICM from drinking water matrices by biotransformation, direct photolysis, ozonation and advanced oxidation processes (AOPs) has been reported in the literature (Kormos et al., 2011; Hapeshi et al., 2013; Chan et al., 2010; Kovalova et al., 2013; Kwon et al., 2012). However, the performance of ICM degradation by these technologies is still under debate. Highly substituted aromatic compounds such as ICM are reported to be difficult to oxidise and even recalcitrant towards ozonation (Hollender et al., 2009). It was also found that only partial oxidation of ICM can be achieved by ozonation, while TiO_2 photocatalysis was effective for quickly removing iopamidol, iopromide and diatrizoate (Murgolo et al., 2015) while it did not lead to complete mineralization of iomeprol (Doll and Frimmel, 2004). In terms of ICM removal, the use of UV/H_2O_2, $UV/S_2O_8^{2-}$, UV/TiO_2 and O_3/H_2O_2 has been investigated (Chu et al., 2011; Huber et al., 2003). Nevertheless, among the proposed ICM treatment technologies, AOPs have shown great potential to degrade these bio-refractory organics and recalcitrant compounds (Migliorini et al., 2011). Thus, it is essential that alternative treatment technologies are developed that can effectively degrade these compounds. In this context, electrochemical technologies, which have been widely recognised as highly efficient for the treatment of recalcitrant wastewaters, offer an alternative solution to other AOP treatments (Abbas et al., 2009; Bashir et al., 2009; Panizza and Cerisola, 2009; Vlyssides et al., 2003). Typically, electrochemical degradation is superior to other treatment technologies due to its versatility, energy efficiency, absence of sludge production and possibility for automation (Zhao et al., 2010).

This work investigates the electrochemical degradation performance of six ICM compounds in bench-scale with synthetic water matrices as well as the occurrence of degradation by-products. To date, the identity and relevance of ICM degradation by-products, which can be formed during the treatment of water matrices, have rarely been investigated (Kormos et al., 2010). To the best of the authors' knowledge, there are few works dealing with the topic at the hand. Zwiener et al. (2009) have studied the iomeprol degradation using a working electrode in nickel foam with an electrolytic cell in which the anodic and cathodic sections are separated by a Nafion septum. Also, Radjenovic et al. (2013) have employed a cell divided by an exchange membrane with a palladium nanoparticles-doped graphite felt working electrode for the study of diatrizoate degradation. While, Mu et al. (2011) have implemented a bioelectrochemical system for the treatment of iopromide with the anode compartment fed with acetate. Furthermore, Eversloh et al. (2014) studied the iopromide in split cells employing a niobium plate coated with a boron-doped diamond film working electrode in order to treat reverse osmosis concentrates from wastewater. In this paper, authors study a wider range of molecules, including iopamidol, iobitridol, iodixanol and iopromide in conventional electrolytic cell. To the best of the authors' knowledge, these molecules have not yet been studied. Molecules have been compared by removal efficiency, energy consumption, degradative pathways and toxicity for each experimental conditions tested. In addition, in this work, we used two DSA® electrodes (titanium coated with a proprietary and patented mixed metal oxide solution of precious metals such Iridium, Ruthenium, Platinum, Rhodium, Tantalum) provided by De Nora Spa (Italy) that have never before been used for applications like that.

Thanks to their specific characteristics, the coating formulation and the coating techniques, the use of DSA® anodes can range from the long established application in the chlor-alkali industry to a wider range of other uses. Moreover, potential future change-overs involve to obtain efficient systems easily extensible to applications at full scale.

2. Materials and methods

2.1. Chemicals

Iopamidol (IOP), iobitridol (IOB), iodixanol (IOX), iopromide (IOPR), amidotrizoate (AMI) and iomeprol (IOMPR) were used as model compounds (see Table 1). The compounds were purchased from Sigma Aldrich and reported to be of high purity (at least 99%). The solvents and buffers used in liquid chromatography with mass spectrometric detection, namely, methanol, acetonitrile and acetic acid were of analytical grade or LC-MS grade.

2.2. ICM containing test solutions

Stock solutions of iopamidol (IOP), iobitridol (IOB), iodixanol (IOX), iopromide (IOPR), amidotrizoate (AMI) and iomeprol (IOMPR) were singularly prepared using deionised water, sodium sulphate or sodium perchlorate in order to obtain a conductivity of 9 mS/cm and to obtain a final concentration of 1 mg/L or 70 mg/L. The higher contrast medium concentration has enabled analysis of parameters that, for the intrinsic sensitivity of the analytic methods, would not be possible to determine at lower concentrations. The test solutions were treated in a lab-scale electro-degradation setup that is described in the following section.

2.3. Electro-degradation reactor

The experimental trials were conducted using a working volume equal to 1 L of a solution containing 1 mg/L or 70 mg/L of the contrast medium to be studied and the supporting electrolyte (sodium perchlorate or sodium sulphate) in order to get a conductivity of 9 mS/cm. Batch electrochemical experiments were performed in a rectangular electrolytic reactor (glass) (see Figure S1) containing 1 L solution. Electrolysis tests were performed under constant current conditions using a direct current (DC) power supply (model SPS-1820, Good Will Instrument Co., Ltd, Taiwan). Two DSA® electrodes (titanium coated with a proprietary and patented mixed metal oxide solution of precious metals such as iridium, ruthenium, platinum, rhodium and tantalum) provided by De Nora S.p.a. (Italy) were arranged parallel to each other and submerged in the synthetic wastewater. Electrode polarity was reversed after each experiment in order to avoid electrode deterioration phenomena. The geometric surface area of each electrode was 110 cm^2. A magnetic stirrer (Model SM 26, Stuart Scientific, Stone, Staffordshire ST15 0SA, UK) was used for mixing of the solution. The inter-electrode distance was 0.5 cm. The temperature was maintained constant (25 °C) by dipping the reactor in a thermostatic bath.

2.4. Analytical methods

Iodide released by the electrochemical reaction of ICM, sulphate and perchlorate was quantified by ion-chromatography (DX-600, Dionex) with a UV or conductivity detector. Molecular iodine was determined using an amperometric titration method (Rice et al., 2012). Iodate ion determination was performed by UPLC-MS analysis (Applied Biosystems/ MSD Sciex). DOC was measured by a TOC-V carbon analyser (Shimadzu). Conductivity and pH were measured on-line using selective probes. The specific energy consumption (E_c, in kWh m^{-3}) was calculated as follows: $E_c = (U_{cell} \times I \times t) / (V \times 3600)$, where U_{cell} is the average cell voltage (V), I is the current (A), t is the electrolysis time (s) and V is the volume of the treated wastewater (L) (Migliorini et al., 2011; Panizza et al., 2010). For