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Electrochemical oxidation of iodinated X-ray contrast media by boron-doped diamond electrodes

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ABSTRACT

Iodinated X-ray contrast media (IXCM) represent widespread water pollutants due to their poor elimination by common wastewater treatment techniques such as aerobic and anaerobic biodegradation. In this study, we demonstrate the removal of six IXCM (iotalamic acid, iopamidol, iohexol, iopromide, iomeprol and diatrizoate) by electrochemical treatment with boron-doped diamond electrodes. Experiments were performed with model solutions and field water samples. Electrochemical treatment of IXCM in synthetic solution resulted in complete deiodination and generation of the oxidation product iodate. We observed a dissolved organic carbon (DOC) decrease of 30%–80% in IXCM solutions, indicating partial mineralisation. Electrochemical IXCM degradation followed pseudo-first-order kinetics. In experiments with surface water and effluent from a wastewater treatment plant, successful degradation of IXCM was achieved despite the high DOC background. These results demonstrate that electrochemical treatment is a promising method for IXCM removal. Further studies into biodegradation of transformation products are recommended.

Keywords: Electrochemical oxidation; Iodinated X-ray contrast media; Boron-doped diamond electrodes

1. Introduction

Persistent pharmaceutical residues are often detected in aquatic environments because of their widespread use and incomplete removal in wastewater treatment plants (WWTPs) [1]. Therefore, alternative processes are required to remove these compounds.

This work focuses on the group of iodinated X-ray contrast media (IXCM), which enable selective display and visualisation of organs and vessels, and therefore, represent the most widely used pharmaceuticals for intravascular application [2]. The usual dose is 50–200 g IXCM per patient, and globally, a total of 3,500 tonne is applied per year [2]. Since, the human organism does not metabolise IXCM and excretes them unchanged within 24 h [2], hospitals and private households are the main contamination sources. Because of their persistence, poor biodegradability [3] and low adsorptive properties, IXCM are difficult to remove from the water cycle.

Different studies reported IXCM in concentrations between ng/L and µg/L in surface water, groundwater and drinking water [3–6]. During drinking water disinfection with chlorine, IXCM can be transformed into genotoxic and cytotoxic iodinated disinfection by-products [7].

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In this study, we investigated electrochemical water treatment as a new approach for IXCM transformation. Boron-doped diamond (BDD) electrodes were selected because of their high chemical, mechanical and thermal stability as well as a high overvoltage at the electrode surface [8]; they are, therefore, particularly suitable for electrochemical treatment of persistent substances such as perfluorinated compounds [9]. We selected the most commonly used six IXCM (diatrizoate, iotalamic acid, iopromide, iohexol, iopamidol and iomeprol). We conducted experiments focusing on formation of iodate, degree of mineralisation and transformation kinetics in different water matrices.

2. Materials and methods

2.1. Chemicals and field samples

All chemicals were analytical grade (≥98%). Diatrizoate sodium was purchased from Sigma-Aldrich Co., (St. Louis, USA), iotalamic acid and iopromide from USP (Rockville, USA), iohexol from LGC (London, UK), iopamidol and iomeprol from Dr. Ehrenstorfer (GmbH, Augsburg, Germany) and Na_2SO_4 from Carl Roth (Karlsruhe, Germany). Table 1 shows the structures and molecular weights of the six tested IXCM.

WWTP effluent and surface water samples were used as field water samples. Initial concentrations of the analysed IXCM were between 80 and 30,000 ng/L.

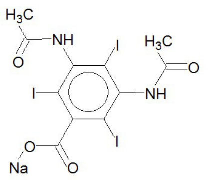
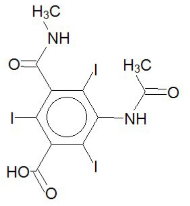
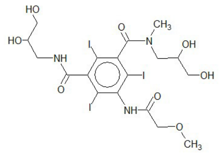
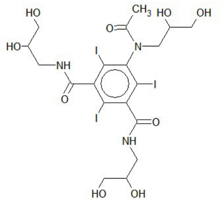
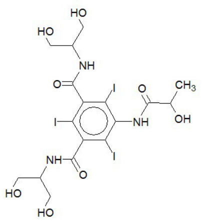
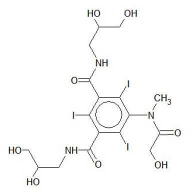
2.2. Experimental setup

Electrochemical oxidation in batch mode was conducted galvanostatically by using an electrochemical cell with internal dimensions of 21 × 7 × 7 cm (as described in reference [9]). We used commercially available Nb/BDD electrodes (DiaChem®, CONDIAS (GmbH, Itzehoe, Germany)) with a geometric area of 32 cm^2; electrode distance varied between 5 (experiments with synthetic medium and wastewater effluent) and 10 cm (experiments with surface water). In order to focus on the oxidation processes at the anode surface, the cell was separated with a bipolar membrane (Fumasep®, Fumatech, Germany) into an anode and a cathode chamber. For continuous mixing of the liquid, two magnetic stirrers were used (500 rpm) and as power source, we deployed the potentiostat/galvanostat PGU OEM-2A-MI (IPS, Germany). Experiments were performed at room temperature (approximately 20°C) in a volume of 1 L. Current density was adjusted to a value between 0.31 and 0.94 mA/cm^2 and treatment time varied between 7 and 72 h. Prior to each experimental run, a onetime polarity change of the BDD electrode was carried out for 30 min in a 0.01 M Na_2SO_4 solution to clean the BDD electrode surface. Table 2 summarises the experimental conditions. The six IXCM (diatrizoate, iotalamic acid, iopromide, iohexol, iopamidol and iomeprol) were tested in synthetic media (0.01 M Na_2SO_4 solution); initial concentrations of the tested substances were between 15 and 25 mg/L. In subsequent experiments, WWTP effluent and surface water were used, with initial concentrations in the µg/L range. The experiments with field water samples were conducted in an undivided cell to simulate practical conditions.

2.3. Analytical methods

In the spiked experiments, IXCM were analysed via liquid chromatography (LC) using a diode array detector (Agilent 1200 equipped with a Phenomenex Gemini 5u C18 110 A 250 × 2 mm column) with a limit of quantification (LOQ) of 0.1 mg/L via direct injection of aqueous samples. Non-spiked field water samples were analysed via LC (Agilent 1290) and a mass spectrometric detector (MS, Sciex API5500) equipped with a Restek Ultra Aromax 3 µm 150 × 2.1 mm; LOQ was 5 ng/L. Samples were concentrated by solid phase extraction. Concentrations of iodide (I^-), chloride (Cl^-) and sulphate ions (SO_4^{2-}) in aqueous solution were determined by ion chromatography (Metrohm

Table 1
Structures and molecular weight (MW) of the six used iodinated X-ray contrast media

IXCM	Chemical structure[a]	MW[a] (g/mol)
Diatrizoate sodium		613.9
Iotalamic acid		613.9
Iopromide		791.1
Iohexol		821.1
Iopamidol		777.1
Iomeprol		777.1

[a] Reference [10].

Table 2
Experimental conditions: initial concentrations of IXCM in WWTP effluent and surface water represent the sum of analysed IXCM

Water matrix	Initial concentration of IXCM (mg/L)	Initial DOC (mg/L)	Conductivity (µS/cm)	Initial pH	Electrolysis duration (h)
Synthetic solution	15–25	4–6	2,000	6–8	7–16
WWTP effluent	0.02	10	950	7	16
Surface water	0.002	2	440	8	72

761 compact IC, Metrohm, Filderstadt, equipped with a Metrohm A-Supp-5 column conductivity detector); LOQ was 1 mg/L. Formation of iodate was determined by IC-ICP-MS (ICS3000, Thermo Fisher Scientific (Massachusetts, USA), equipped with a Dionex IonPac AG16 [4 × 250 mm] column, coupled with ICP-MS Agilent 7700); LOQ was 0.5 mg/L using direct injection of aqueous samples. Dissolved organic carbon (DOC) was analysed using an Elementar vario TOC cube (LOQ: 0.2 mg/L).

3. Results and discussion

3.1. Electrochemical oxidation in synthetic solution

We studied the elimination of elevated IXCM concentrations in a synthetic solution using electrochemical oxidation. All tested IXCM could be eliminated by electrochemical oxidation with BDD electrodes. After 16 h of electrolysis under galvanostatic conditions (10 mA), degradation of at least 90% was achieved for all six IXCM in separate experiments (Fig. 1). Two different degradation scenarios have to be considered after anodic oxidation: organic compounds are partially oxidised (electrochemical conversion) or transformed into water, carbon dioxide and other inorganic components through electrochemical combustion [11]. To examine the degree of electrochemical mineralisation, we measured DOC removal and observed that DOC decreased in all experiments, but was still detectable. High mineralisation rates of 60%–80% were obtained for diatrizoate, iotalamic acid, iopamidol, iohexol and iopromide. However, DOC decrease was low for iomeprol, indicating the formation of organic transformation products (Fig. 1).

The basic structure of IXCM is 2,4,6-triiodobenzene with three iodine atoms. During electrochemical degradation, dehalogenation of IXCM occurs, resulting in the possible generation of three different forms of iodine. In order to demonstrate that oxidation has occurred, we measured iodate and iodide concentrations. In the anode compartment, iodide concentration after electrochemical oxidation was below LOQ (1 mg/L) for all tested IXCM (Fig. 2). A theoretical maximum iodate concentration was calculated based on the measured degradation of the tested IXCM and compared with the measured concentration in the solution after electrochemical oxidation. The results show that iodate was the main product of dehalogenation (Fig. 2), which confirms the occurrence of deiodination processes previously reported, e.g., diatrizoate and iopromide in studies using different electrochemical cells [12–14]. In our study, we obtained similar results for the six IXCM, demonstrating efficient deiodination and iodate formation independent of the different IXCM molecular structures (Table 1).

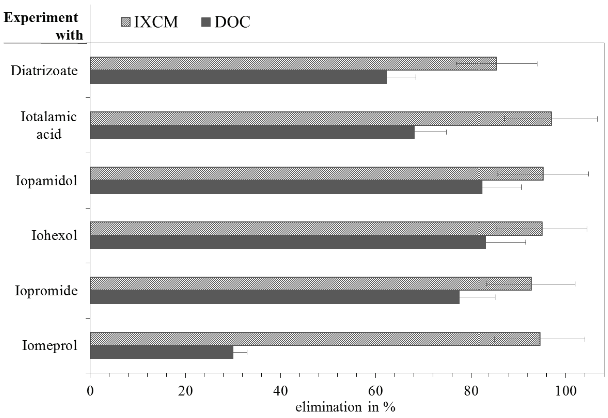


Fig. 1. Electrochemical degradation of six iodinated X-ray contrast media (IXCM) in synthetic solution and decrease of dissolved organic carbon (DOC) after electrochemical treatment. Error bars represent the absolute analytical error of 10%.

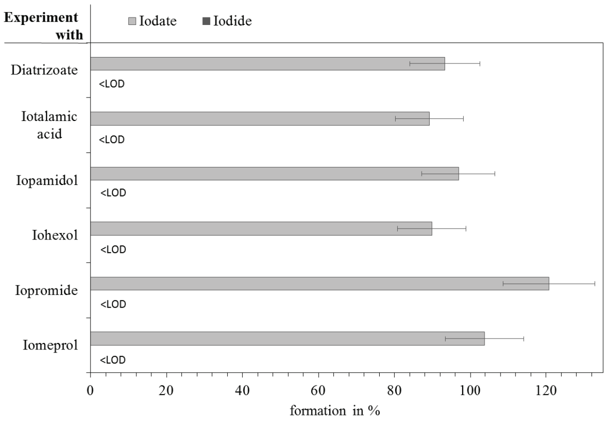


Fig. 2. Formation of iodide and iodate by electrochemical oxidation, calculated based on the measured concentration in the solution after electrochemical oxidation compared with the theoretical maximum concentration calculated from the degradation of tested iodinated X-ray contrast media (Fig. 1). Error bars represent the absolute analytical error of 10%.

We observed exponential degradation kinetics of all six tested IXCM, which is in agreement with the results of previous studies [12,13,15]. The pseudo-first-order rates were determined from a linear plot of ln(c/c_0) against time and are shown in Table 3 in comparison with the rates from previous studies. In this study, reaction rates for iotalamic acid were five times higher than those for iohexol. In previous studies, higher rate constants were explained by better adsorption of more hydrophobic substances on the hydrophobic BDD electrode [9,16]. It has to be noted that pH values between 4 and 5 were observed at the end of the IXCM experiments in synthetic solution. Unfortunately, reliable logK_{ow} data for IXCM as a function of pH are not available. However, electrochemical reaction rates were significantly lower for the IXCM containing three amino groups (iopromide, iohexol, iopamidol, iomeprol) compared with the IXCM with only two amino groups (diatrizoate, iotalamic acid).

In this study, we observed kinetic values in the same order of magnitude as found by Eversloh et al. [13] and Radjenovic et al. [15], despite different experimental conditions. In contrast, Del Moro et al. [12] worked at extremely high current densities and absolute currents of about 7 A, and therefore, reported higher values.

Additional experiments with diatrizoate were conducted with different current densities (Fig. 3). We observed increased elimination with higher current density, confirming its influence on reaction rate. Our results are in agreement with those found by Radjenovic et al. [15].

With regard to electrolysis energy consumption further important aspects are the effects of inter-electrode distance. Since, the ohmic potential drop is proportional to the inter-electrode distance, reducing this distance is of great importance for reducing the electrolysis energy consumption [17]. However, direct electrode contact and clogging have to be avoided. In this study, the focus was on the degradation kinetics of different IXCM and the influence of different current densities; all experiments in synthetic solution had the same inter-electrode distance. Investigations into process efficiency are encouraged.

3.2. Electrochemical treatment of field water samples

The physical–chemical characteristics of the water (nature and concentration of electrolytes, pH value and concentration of target pollutants) affect the electrochemical processes [11]. Therefore, this part of the study focused on IXCM removal in water samples with high DOC background. After electrochemical treatment of WWTP effluent under identical conditions described for the previous experiments with synthetic solutions (galvanostatic, 10 mA and 16 h), degradation beyond 90% was observed for all analysed IXCM (Fig. 4(a)). As demonstrated by the high initial DOC values, WWTP effluent had a high background of other organic compounds. During electrolysis, DOC was reduced by 43% and IXCM in surface water samples with high DOC values were treated. We observed IXCM removal from contaminated surface waters despite initial IXCM concentrations below 600 ng/L (Fig. 4(b)). The observed DOC removal of 78% from 2.2 to 0.48 mg/L showed a mineralisation rate of 78% of the organic compounds.

Our results show that electrochemical transformation occurred in the presence of high DOC background levels (2–10 mg/L), resulting in high DOC/IXCM ratios in the different field water matrices. All tested IXCM could successfully be removed under natural conditions; however, in terms of energy consumption, the treatment of highly concentrated IXCM is more efficient due to pseudo-first-order rate kinetics.

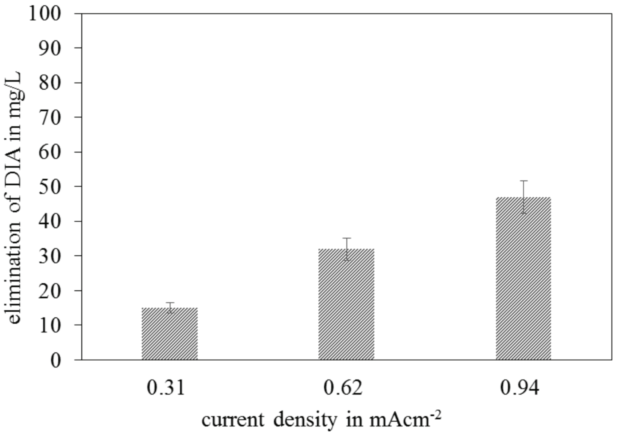


Fig. 3. Elimination of diatrizoate (DIA) influenced by different current densities. Error bars represent the absolute error of 10% from high performance liquid chromatography analytics.

Table 3
First-order rate constants of tested IXCM in comparison with previous studies

IXCM	First-order rate constant	Experimental condition	Reference
Diatrizoate	0.4×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
	0.7×10^{-4} s^{-1}	3.7 mS/cm (KH_2PO_4/K_2HPO_4), 3.5 V	[15]
	2.2×10^{-4} s^{-1}	9 mS/cm (Na_2SO_4), 64 mA/cm^2	[12]
Iotalamic acid	0.5×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
Iopamidol	0.2×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
	2.5×10^{-4} s^{-1}	9 mS/cm (Na_2SO_4), 64 mA/cm^2	[12]
Iohexol	0.1×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
Iopromide	0.3×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
	0.6×10^{-4} s^{-1}	0.25 g/L Na_2SO_4, 1.7 mA/cm^2	[13]
	2.0×10^{-4} s^{-1}	9 mS/cm (Na_2SO_4), 64 mA/cm^2	[12]
Iomeprol	0.3×10^{-4} s^{-1}	2 mS/cm (Na_2SO_4), 0.31 mA/cm^2	This study
	2.3×10^{-4} s^{-1}	9 mS/cm (Na_2SO_4), 64 mA/cm^2	[12]

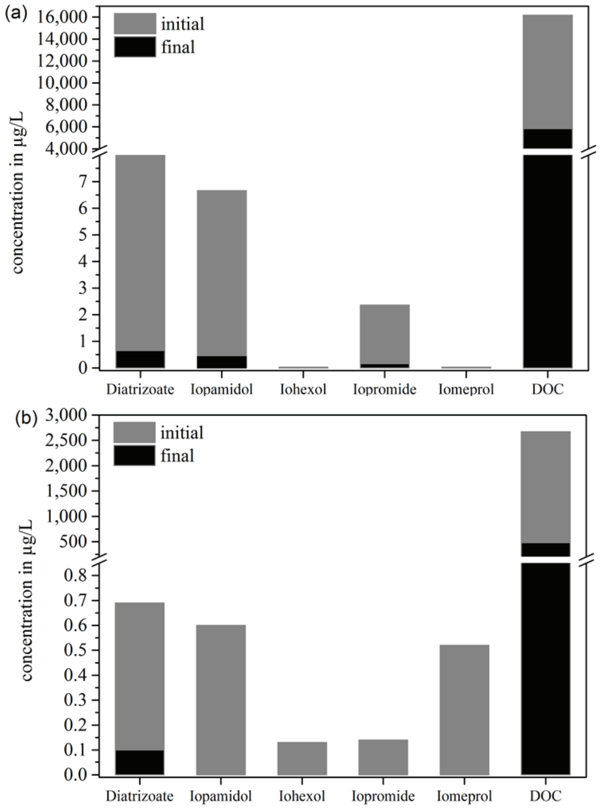


Fig. 4. Electrochemical degradation of IXCM and DOC concentrations before and after treatment in: (a) WWTP effluent (10 mA, 16 h) and (b) surface water (25 mA, 72 h).

4. Conclusion

This study demonstrated that electrochemical treatment with BDD electrodes could be an effective removal method for IXCM. We showed the degradation of six IXCM in synthetic solution. Hereby, inorganic iodine species are useful parameters to indicate IXCM degradation mechanisms. Oxidative deiodination occurred in the anode chamber, as demonstrated by iodate formation in the synthetic solution. Pseudo-first-order kinetics were observed for all six tested IXCM. Degradation efficiency can be controlled depending on current density and treatment time. Successful electrochemical transformation of IXCM could also be demonstrated for WWTP effluent with a high DOC background (ratio DOC/IXCM up to 500) as well as surface water with a DOC/IXCM ratio of up to 5,000. In all experiments, decrease of DOC was observed, indicating partial mineralisation.

In conclusion, electrochemical oxidation with BDD electrodes represents a promising approach for ICXM removal. Based on our results, further studies into process efficiency are encouraged. In particular, toxicity and biodegradability of electrochemical transformation products should be considered.

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