

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 waste water treatment techniques such as aerobic and anaerobic biodegradation. In this study, we demonstrate the removal of six IXCM (iotalamic acid, iopamidol, iohexol, iopromide, iomeprol, 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 DOC decrease of 30 to 80% in IXCM solutions, indicating partial mineralisation. Electrochemical IXCM degradation followed pseudo first-order kinetics. In experiments with surface water and effluent from a waste water treatment plant, successful degradation of IXCM was achieved despite the high DOC background. These results demonstrate that electrochemical treatment is a promising method for iodinated X-ray contrast media removal. Further studies into biodegradation of transformation products are recommended.

Keywords

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

INTRODUCTION

Persistent pharmaceutical residues are often detected in aquatic environments because of their widespread use and incomplete removal in waste water treatment plants (WWTP) (Kümmerer, 2004). 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 (Pérez and Barceló, 2007). The usual dose is 50 to 200 g IXCM per patient, and globally, a total of 3,500 t is applied per year (Pérez and Barceló, 2007). Since the human organism does not metabolise IXCM and excretes them unchanged within 24 hours (Pérez and Barceló, 2007), hospitals and private households are the main contamination sources. Because of their persistence, poor biodegradability (Tiehm et al., 2011) 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, ground water and drinking water (Seitz et al., 2006; Sacher et al., 2001; UBA 2011, Tiehm et al., 2011). During drinking water disinfection with chlorine, IXCM can be transformed into genotoxic and cytotoxic iodinated disinfection by-products (Duirk et al. 2011).

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 (Tröster et al., 2004); they are therefore particularly suitable for electrochemical treatment of persistent substances such as perfluorinated compounds (Trautmann et al., 2015). 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.

MATERIALS AND METHODS

Chemicals and field samples

All chemicals were analytical grade ($\geq 98\%$). Diatrizoate sodium was purchased from Sigma Aldrich Co, iotalamic acid and iopromide from USP, iohexol from CRS, iopamidol and iomeprol from Dr. Ehrenstorfer and Na_2SO_4 from Carl Roth. Table 1 shows the structures and molecular weights of the six tested IXCM.

Waste water treatment plant (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.

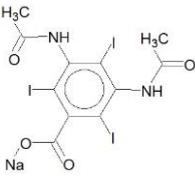
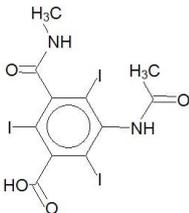
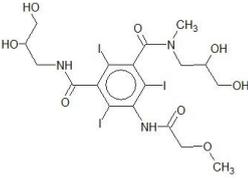
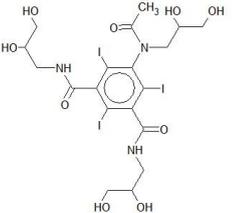
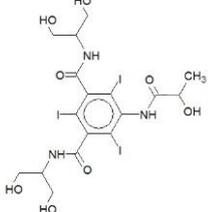
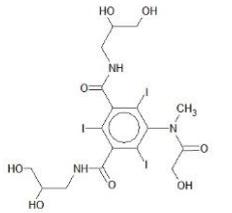
Experimental setup

Electrochemical oxidation in batch mode was conducted galvanostatically by using an electrochemical cell with internal dimensions of 21x7x7 cm (as described in Trautmann et al., 2015). We used commercially available Nb/BDD electrodes (DiaChem®, CONDIAS) with a geometric area of 32 cm²; electrode distance varied between 5 and 10 cm. 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 mAcm⁻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 minutes 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, waste water treatment plant (WWTP) effluent and surface water were used, with initial concentrations in the $\mu\text{g/L}$ range. The experiments with field water samples were conducted in an undivided cell to simulate practical conditions.

Analytical methods

In the spiked experiments, IXCM were analysed via liquid chromatography (LC) using a diode array detector (DAD) (Agilent 1200 equipped with a Phenomenex Gemini 5u C18 110 A 250x2 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 150x2.1 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 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, ThermoFisher Scientific, equipped with a Dionex IonPac AG16 (4x250 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).

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

IXCM	Chemical structure ¹	MW ¹ in g/mol
Diatrizoate Sodium (DIA)		613.9
Iotalamic acid (IOA)		613.9
Iopromide (IOPR)		791.1
Iohexol (IOX)		821.1
Iopamidol (IOPA)		777.1
Iomeprol (IOM)		777.1

¹SRC PhysProp Database, 2016

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 in mg/L	Initial DOC in mg/L	Conductivity in $\mu\text{S/cm}$	Initial pH	Electrolysis duration in 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

RESULTS AND DISCUSSION

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 hours of electrolysis under galvanostatic conditions (10 mA), degradation of at least 90% was achieved for all six IXCM in separate experiments (Figure 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 (Anglada et al., 2009). 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 to 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 (Figure 1).

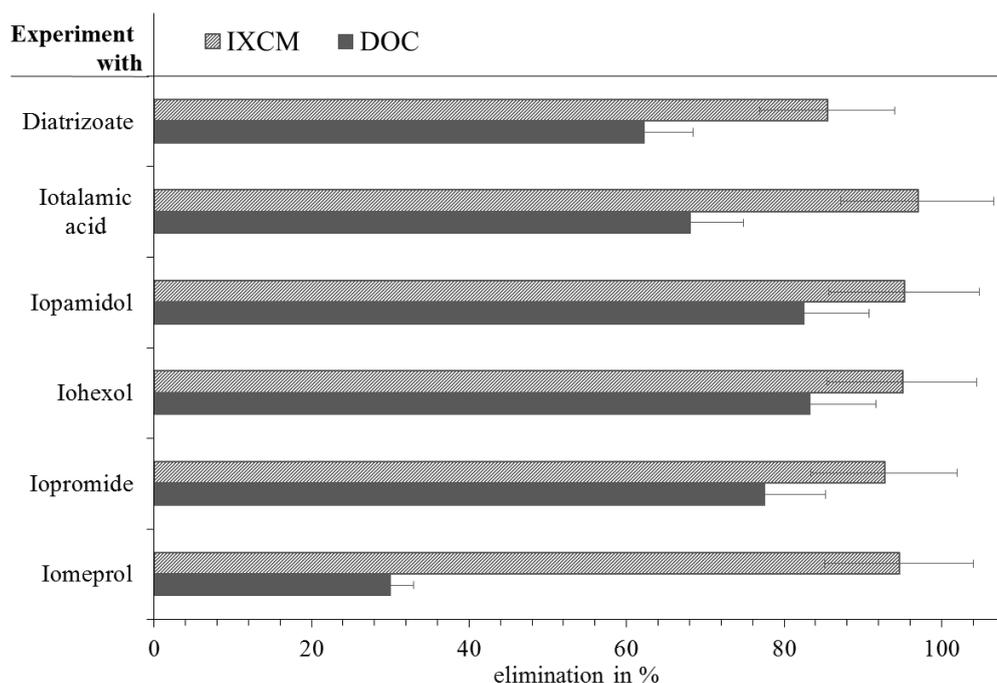


Figure 1. Electrochemical degradation of six iodinated X-ray contrast media (IXCM) in synthetic solution and decrease of dissolved organic carbon (DOC) after electrochemical treatment. Error bars represent the absolute analytical error of 10%.

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 (Figure 2). A theoretical maximum iodate concentration was calculated based on the measured degradation of the tested IXCM and compared to the measured concentration in the solution after electrochemical oxidation. The results show that iodate was the main product of dehalogenation (Figure 2), which confirms the occurrence of deiodination processes previously reported for e.g. diatrizoate and iopromide in studies using different electrochemical cells (Del Moro et al., 2015; Eversloh et al., 2014; Zwiener et al., 2009). 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).

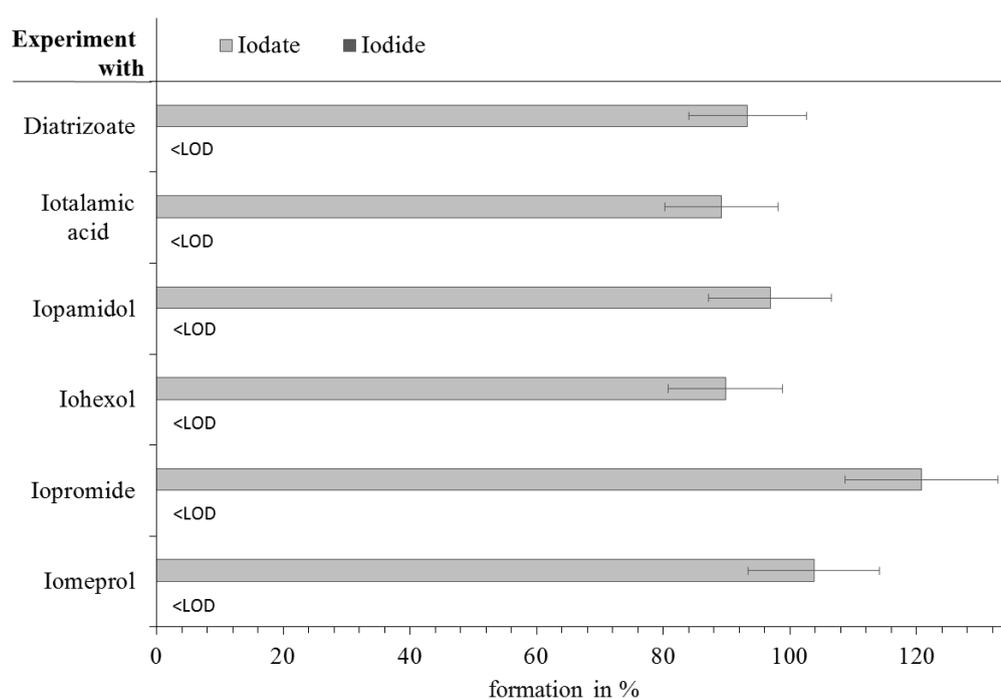


Figure 2. Formation of iodide and iodate by electrochemical oxidation, calculated based on the measured concentration in the solution after electrochemical oxidation compared to the theoretical maximum concentration calculated from the degradation of tested iodinated X-ray contrast media (Figure 1). 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 (Radjenovic et al., 2013, Eversloh et al., 2014; Del Moro et al., 2015). 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 (Zhou et al., 2012; Trautmann et al., 2015). 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 $\log K_{ow}$ 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 to 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. (2014) and Radjenovic et al. (2013), despite different experimental conditions. In contrast, Del Moro et al. (2015) worked at extremely high current densities and absolute currents of about 7 A and therefore reported higher values.

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

IXCM	First-order rate constant	Experimental condition	Reference
Diatrizoate	$0.4 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
	$0.7 \cdot 10^{-4} \text{ s}^{-1}$	3.7 mS/cm ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$), 3.5 V	Radjenovic et al., 2013
	$2.2 \cdot 10^{-4} \text{ s}^{-1}$	9 mS/cm (Na_2SO_4), 64 mA/cm ²	Del Moro et al., 2015
Iotalamic acid	$0.5 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
Iopamidol	$0.2 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
	$2.5 \cdot 10^{-4} \text{ s}^{-1}$	9 mS/cm (Na_2SO_4), 64 mA/cm ²	Del Moro et al., 2015
Iohexol	$0.1 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
Iopromide	$0.3 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
	$0.6 \cdot 10^{-4} \text{ s}^{-1}$	0.25 g/L Na_2SO_4 , 1.7 mA/cm ²	Eversloh et al., 2014
	$2.0 \cdot 10^{-4} \text{ s}^{-1}$	9 mS/cm (Na_2SO_4), 64 mA/cm ²	Del Moro et al., 2015
Iomeprol	$0.3 \cdot 10^{-4} \text{ s}^{-1}$	2 mS/cm (Na_2SO_4), 0.31 mA/cm ²	This study
	$2.3 \cdot 10^{-4} \text{ s}^{-1}$	9 mS/cm (Na_2SO_4), 64 mA/cm ²	Del Moro et al., 2015

Additional experiments with diatrizoate were conducted with different current densities (Figure 3). We observed increased elimination with higher current density, confirming its influence on reaction rate. Our results are in agreement with those found by Del Moro et al. (2015).

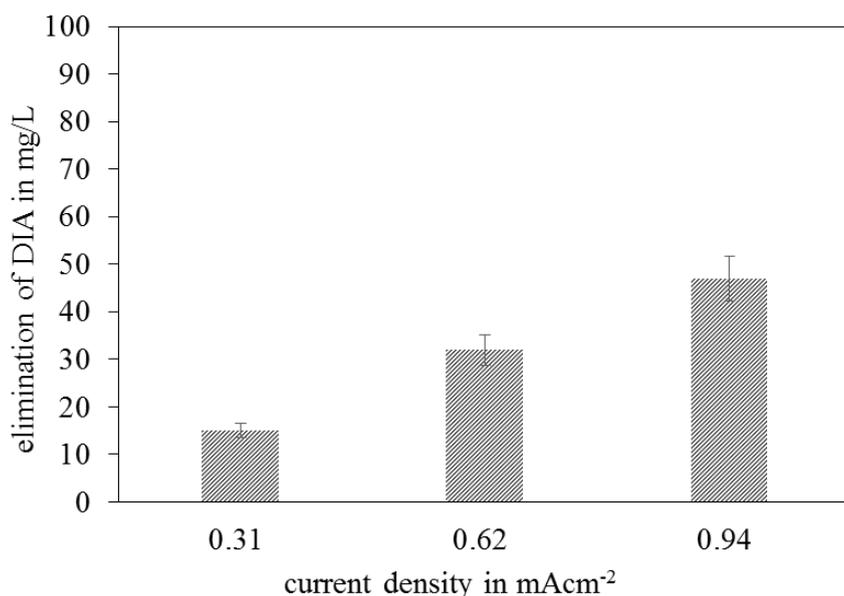


Figure 3. Elimination of diatrizoate (DIA) influenced by different current densities. Error bars represent the absolute error of 10% from HPLC analytics.

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 (Anglada et al., 2009). 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 (Figure 4a). 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 (Figure 4b). The observed DOC removal of 78% from 2.2 mg/L to 0.48 mg/L showed a mineralisation rate of 78% of the organic compounds.

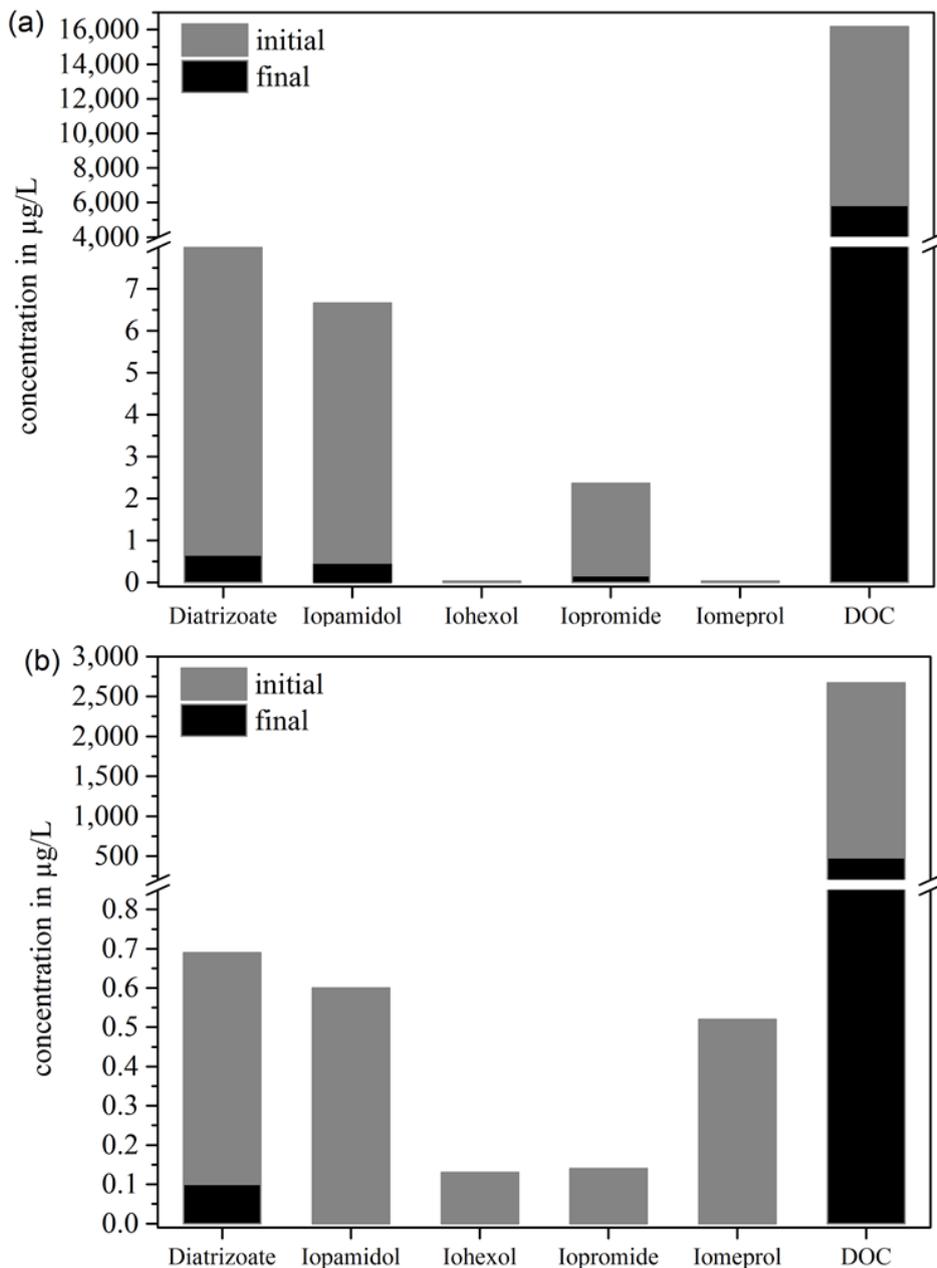


Figure 4. Electrochemical degradation of IXCМ and DOC concentrations before and after treatment in (a) WWTP effluent (10 mA, 16 h) and (b) surface water (25 mA, 72 h).

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

CONCLUSION

This study demonstrated that electrochemical treatment with BDD electrodes could be an effective removal method for IXCМ. We showed the degradation of six IXCМ in synthetic solution. Hereby, inorganic iodine species are useful parameters to indicate IXCМ 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 IXCM removal. Based on our results, further studies into process efficiency are encouraged. In particular, toxicity and biodegradability of electrochemical transformation products should be considered.

ACKNOWLEDGEMENT

Financial support from the German Ministry of Education and Research (BMBF, grant no 02WER1315B) is gratefully acknowledged. We thank Dr. K.-M. Mangold and S. Hild (DFI, DECHEMA, Frankfurt, Germany) for stimulating discussions.

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