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# Electrochemical treatment of iopromide under conditions of reverse osmosis concentrates – Elucidation of the degradation pathway

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## ABSTRACT

Application of reverse osmosis for the reuse of treated wastewater on the one hand offers a way to provide high quality effluent waters. On the other hand reverse osmosis concentrates exhibiting highly concentrated contaminants are produced simultaneously. Electrochemical treatment of those concentrates is regarded as one possible answer to the problem of their disposal into surface waters. Nevertheless, due to the diversity of direct and indirect degradation processes during electrolysis, special care has to be taken about the formation of toxic transformation products (TPs). In this study the electrochemical transformation of the X-ray contrast medium iopromide was investigated as a representative of biologically persistent compounds. For this purpose, anodic oxidation at boron doped diamond as well as cathodic reduction using a platinum electrode were considered. Kinetic analyses revealed a transformation of 100  $\mu\text{M}$  iopromide with first order kinetic constants between 0.6 and  $1.6 \times 10^{-4} \text{ s}^{-1}$  at the beginning and a subsequent increase of the reaction order due to the influence of secondary oxidants formed during electrolysis. Mineralization up to 96% was achieved after about 7.5 h. At shorter treatment times several oxidatively and reductively formed transformation products were detected, whereas deiodinated iopromide represented the major fraction. Nevertheless, the latter exhibited negligible toxicological relevance according to tests on vibrio fisheri. Additional experiments utilizing a divided cell setup enabled the elucidation of the transformation pathway, whereas emerging TPs could be identified by means of high resolution mass spectrometry and  $\text{MS}^n$ -fragmentations. During electrolysis the iodine released from iopromide was found to 90% as iodide and to 10% as iodate even in the open cell experiments, limiting the potential formation of toxic iodo-disinfection by-products. Chlorinated TPs were not found.

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## 1. Introduction

Considering the growing demand for fresh water world-wide due to limited water resources, especially in dry regions, the

reuse of treated wastewater is becoming a major topic in environmental sciences (Grant et al., 2012; Norton-Brandão et al., 2013). In this context, reverse osmosis (RO) has shown to be capable of removing more than 95% of contaminants

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when applied as a final step after conventional wastewater treatment (Kegel et al., 2010; Cartagena et al., 2013). Nevertheless, the treatment and subsequent disposal of the generated RO concentrates often remains an unsolved question. The RO concentrates are frequently disposed into surface waters without any treatment, although the concentrations of the organic and inorganic contaminants or pathogens can be 6–7 fold higher than in the original wastewater (Chelme-Ayala et al., 2009; Malaeb and Ayoub, 2011; Pérez-González et al., 2012). Among the vast number of natural and anthropogenic substances, iodinated contrast media (ICM) represent a major class of pharmaceuticals frequently passing conventional wastewater treatment plants to an appreciable extend and are therefore present in secondary effluents and surface waters at concentration levels up to 16 µg/L and 2.8 µg/L, respectively (Ternes and Hirsch, 2000; Seitz et al., 2006; Fono and Sedlak, 2007; Schulz et al., 2008; Kormos et al., 2011). In reverse osmosis concentrates about 7 µg/L have been reported (Benner et al., 2008). In order to cope with those emerging contaminants, different abatement strategies are currently under discussion. Promising techniques in this regard are advanced oxidation processes (AOPs), which utilize *in-situ* generated highly reactive hydroxyl radicals. (Abdelmelek et al., 2011; Gur-Reznik et al., 2011; Pérez-González et al., 2012) In case of reverse osmosis concentrates a subsequent electrochemical treatment using boron doped diamond (BDD) electrodes offers a potential removal of contaminants, since electrolysis itself profits from enhanced electrical conductivity due to their high salinity and BDD is also capable to generate hydroxyl radicals. (Marselli et al., 2003; Van Hege et al., 2004; Pérez et al., 2010) However, care has to be taken regarding the formation of secondary oxidants such as active chlorine, which might lead to undesired transformation products (TPs) (Wang and Farrell, 2004; Martinez-Huitle and Ferro, 2006; Deborde and von Gunten, 2008; Bagastyo et al., 2012). It is already reported that electrochemical treatment of solutions with high chloride content facilitates the formation of chlorinated disinfection by-products (DBPs) (Deborde and von Gunten, 2008; Bergmann et al., 2009; Anglada et al., 2011). Furthermore, Duirk et al. showed that the chlorination of ICM-containing waters might lead to even more toxic iodinated DBPs such as Iodo-THMs and Iodo-acids (Duirk et al., 2011).

Within this study the electrochemical degradation behaviour of iopromide was investigated as a representative of biologically persistent compounds. For this purpose special care was taken of emerging TPs as well as of the fate of the iodine released from iopromide.

## 2. Materials and methods

### 2.1. Chemicals and reagents

All chemicals and solvents were of analytical grade (>95%). Iopromide was a courtesy of the Schering AG, Germany. Iopromide-d<sub>3</sub>, which was used as an authentic reference standard, was purchased from Toronto Research Chemicals Inc., Canada. Reverse osmosis concentrates were obtained from a pilot plant in Atlit, Israel, fed by secondary effluents

**Table 1 – Main characteristics of RO concentrate.**

Parameter	Value
pH	8.4
Conductivity (21 °C)	2.60 mS/cm
TOC	17.0 mg/L
TIC	84.4 mg/L
Chloride	150 mg/L
Nitrate	13 mg/L
Phosphate	12 mg/L
Sulphate	114 mg/L

from a conventional wastewater treatment plant. Ultrafiltration of this effluent was performed prior to RO. The main characteristics of the concentrates are provided in Table 1.

### 2.2. Electrolysis setup

Standard electrochemical experiments were conducted in a bulk electrolysis cell (single compartment) consisting of a 100 mL glass beaker equipped with a platinum cathode and a silver/silver chloride reference electrode (BASinc, USA). A rectangular niobium plate (4 × 3 cm) coated with a boron-doped diamond film (Condias, Germany) was used as the working electrode under anodic polarization. Additional studies of the oxidative and reductive reactions were carried out in a custom-built H-cell, whose two cylindrical compartments (3.8 cm diameter) were divided by a nafion membrane of 0.18 mm thickness and an effective area of 2.3 cm<sup>2</sup> (Alfa-Aesar, Germany). According to the single compartment cell, the BDD and reference electrode were used in the anodic compartment, while the platinum electrode was used in the cathodic part. A schematic description of the electrolysis setup is provided in the SI. Current and voltage were controlled by a PGU 20V-2A-E potentiostat (Peter Schrems Elektroniklabor, Germany).

### 2.3. Treatment conditions

Degradation experiments were performed in galvanostatic mode with reverse osmosis concentrates and ultra-pure water containing sodium chloride (0.25 and 2.0 g/L) or sodium sulphate (0.25 g/L) at 21 ± 2 °C. All solutions (75 mL) were spiked with iopromide to yield an effective concentration of 100 µmol/L. For the divided cell, 75 mL were used in each compartment. Stirring was maintained at 500 rpm throughout the whole process using a magnetic stirrer.

### 2.4. Sampling and quantification of analytes

Depending on the treatment conditions, 1.0 mL aliquots of the electrolyzed solutions were sampled at defined time intervals. The samples were immediately quenched with 10 µL of a 5 M sodium thiosulphate solution, to suppress further degradation via secondary oxidants. Analyses were performed by means of LC HR-MS using an Accela HPLC system (Thermo Fisher Sci., Germany) equipped with a high resolution mass analyzer (LTQ Orbitrap Velos, Thermo Fisher Sci., Germany). Separation of the analytes was achieved on a Synergi 4µ Polar RP column using ultra pure water and acetonitrile as eluents.

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