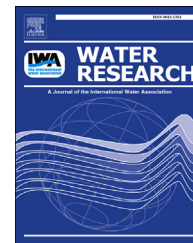




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Electrochemical oxidation of tramadol in low-salinity reverse osmosis concentrates using boron-doped diamond anodes

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ABSTRACT

The electrochemical treatment of low-salinity reverse osmosis (RO) concentrates was investigated using tramadol (100 μM) as a model substance for persistent organic contaminants. Galvanostatic degradation experiments using boron-doped diamond electrodes at different applied currents were conducted in RO concentrates as well as in ultra-pure water containing either sodium chloride or sodium sulfate. Kinetic investigations revealed a significant influence of *in-situ* generated active chlorine besides direct anodic oxidation. Therefore, tramadol concentrations decreased more rapidly at elevated chloride content. Nevertheless, reduction of total organic carbon (TOC) was found to be comparatively low, demonstrating that transformation rather than mineralization was taking place. Early stage product formation could be attributed to both direct and indirect processes, including demethylation, hydroxylation, dehydration, oxidative aromatic ring cleavage and halogenation reactions. The latter led to various halogenated derivatives and resulted in AOX (adsorbable organic halogens) formation in the lower mg/L-range depending on the treatment conditions. Characterisation of transformation products (TPs) was achieved via MSⁿ experiments and additional NMR measurements. Based on identification and quantification of the main TPs in different matrices and on additional potentiostatic electrolysis, a transformation pathway was proposed.

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1. Introduction

Removal of persistent organic contaminants from wastewater has become a major issue in environmental research, especially in view of water reclamation purposes (Grant et al., 2012; Norton-Brandão et al., 2013). Among several different techniques considered to tackle this problem, application of

reverse osmosis (RO) holds promise for almost completely removing both natural and anthropogenic substances (Malaeb and Ayoub, 2011; Cartagena et al., 2013). At the same time, RO brines are generated, containing the initial contaminants in up to 6–7 fold concentration (Chelme-Ayala et al., 2009). In order to minimize the risks posed by such highly contaminated wastewater, various post-treatment methods are currently discussed (Pérez-González et al., 2012). In this

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context electrochemical degradation techniques profit from the enhanced salt content of RO brines, which results in a better electrical conductivity compared to conventional wastewater. Various publications are available up to date, describing the efficiencies of different strategies for the electrochemical oxidation or reduction of organic contaminants (Bagastyo et al., 2011; Radjenovic et al., 2011a, b, 2012, 2013). In the first case, the use of boron doped diamond (BDD) electrodes is regarded as a promising concept, due to their ability to generate highly reactive hydroxyl radicals (Marselli et al., 2003; Pérez et al., 2010; Bagastyo et al., 2012). Those are capable to degrade various contaminants to a large degree (von Sonntag and von Gunten, 2012). Nevertheless, elimination of target substances does not necessarily imply full mineralization and special care has to be taken about the occurrence of transformation products (TPs) formed during the process (Radjenovic et al., 2011a, b; Lütke Eversloh et al., 2014).

The aim of the current study was to investigate the suitability of electrochemical treatment with BDD electrodes to remove emerging pollutants from RO concentrates. For this purpose, we examined the degradation and fate of tramadol (TRA) as a representative for persistent organic contaminants. TRA is an analgesic agent, which is widely applied in both human and veterinary medicine. In 2012, about 24 tons were prescribed only in Germany (Schwabe and Paffrath, 2013). Whereas after medication up to 30% are excreted unchanged via urine, most of it is subject to metabolism, primarily resulting in *N*-desmethyl- (*N*-DES) and *O*-desmethyltramadol (*O*-DES) (Lintz et al., 1981; Chytil et al., 2009). Conventional wastewater treatment plants are often not capable to completely remove those compounds. Thus, considering TRA and *O*-DES, almost 1 µg/L were found in secondary effluents of WWTPs fed from households and hospitals (Rua-Gomez and Püttmann, 2012; Hummel et al., 2006). And although slow photodegradation of TRA in natural rivers was reported (Bergheim et al., 2012; Rúa-Gómez and Püttmann, 2013), concentrations in the range of 100 ng/L were frequently detected in surface waters (Rua-Gomez and Püttmann, 2012). Further studies on TRA elimination addressed the application of advanced oxidation processes (AOPs) as additional step in wastewater treatment. Zimmermann et al. (2011) demonstrated the degradation of TRA during ozonation yielding mainly tramadol-*N*-oxide and *N*-DES. Within the same study they reported an almost completely different transformation pathway if ferrate is applied. However, efficient mineralization could not be achieved in both cases. Irradiation with UV light in the presence of chloramines was reported to result in further TPs again, whereas addition of hydrogen peroxide led to an at least partial removal of DOC (Radjenovic et al., 2012).

Within this manuscript we present the electrochemical degradation of TRA as well as its intermediately occurring TPs. For this purpose, both artificial and real RO brines spiked with TRA were treated in laboratory scale batch experiments applying a BDD anode and a platinum cathode. Since electrochemical treatment of RO brines is capable to form secondary oxidants, such as hypochlorite from chloride (Martinez-Huitle and Ferro, 2006; Pérez-González et al., 2012), special focus was put on the formation of chlorinated by-products.

2. Materials and methods

2.1. Chemicals and reagents

All solvents and commercially available chemicals were at least analytical grade. Tramadol hydrochloride (99%) was purchased from Sigma–Aldrich. Tramadol-*d*₆ (Toronto Research Chemicals), *O*-desmethyl- and *N*-desmethyltramadol hydrochloride (both 1.0 mg/L in methanol, Cerilliant) and Tramadol-*N*-oxide (LGC Standards) were used in mass spectrometry measurements as internal and external standards, respectively.

2.2. Electrolysis setup

Electrochemical degradation experiments were conducted in a 100 mL single compartment bulk electrolysis cell equipped with a platinum cathode and a silver/silver chloride reference electrode (all BASinc, USA). A rectangular BDD electrode (exposed surface area: 25 cm², Condias, Germany) was installed as anode. Experiments in divided cells were conducted using a custom-built H-cell consisting of two cylindrical compartments (3.8 cm diameter). Separation of the compartments was achieved by a 0.18 mm thick nafion membrane with an effective area of 2.3 cm² (Alfa-Aesar, Germany). A more detailed description of both electrochemical cells 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

Electrolysis was conducted in galvanostatic or potentiostatic mode at room temperature. RO concentrates were obtained from a pilot plant in Atlit, Israel, whose influent was supplied by a conventional wastewater treatment plant followed by ultrafiltration. A low-salinity concentrate was used, which mainly consisted of 150 mg/L chlorides, 1 mg/L bromides and 114 mg/L sulfates with a conductivity of $\kappa = 2.60$ mS/cm. An overview about the main characteristics of the RO concentrate is provided in the SI. For mechanistic studies, solutions of sodium chloride (0.25 g/L, $\kappa = 0.52$ mS/cm and 1.0 g/L, $\kappa = 2.02$ mS/cm) or sodium sulfate (0.35 g/L, $\kappa = 0.58$ mS/cm) in ultra-pure water were added. Electrolyses were conducted at approximately neutral pH (NaCl, Na₂SO₄: pH 6–7, RO: pH 8.4). No further pH adjustment (e.g. by adding a buffer) was performed to avoid matrix effects. In all cases 75 mL were used in each compartment (2 × 75 mL for divided cell setup) and tramadol hydrochloride was spiked into the respective matrix. Studies were performed using an effective TRA concentration of 100 µmol/L to facilitate identification and characterization of transformation products. The resulting solution was stirred at 500 rpm during treatment using a PTFE-coated magnetic stirrer bar.

2.4. Sampling and LC-MS analysis

At defined time intervals, 1.0 mL aliquots of the treated solutions were sampled, spiked with 10 µL sodium thiosulfate solution (5 M) to destroy secondary oxidants and stored in

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