



Electrochemical treatment of reverse osmosis concentrate on boron-doped electrodes in undivided and divided cell configurations

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HIGHLIGHTS

- 100% of COD and ~70% of DOC was removed in both cell configurations.
- ~21.7 mg L⁻¹ of AOCl and ~2.3 mg L⁻¹ of AOBr was formed regardless of the membrane use.
- The TEQ was far lower than expected given the high AOCl concentrations.
- The undivided cell consumed lower energy compared to the divided cell.

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ABSTRACT

An undivided electrolytic cell may offer lower electrochlorination through reduction of chlorine/hypochlorite at the cathode. This study investigated the performance of electrooxidation of reverse osmosis concentrate using boron-doped diamond electrodes in membrane-divided and undivided cells. In both cell configurations, similar extents of chemical oxygen demand and dissolved organic carbon removal were obtained. Continuous formation of chlorinated organic compounds was observed regardless of the membrane presence. However, halogenation of the organic matter did not result in a corresponding increase in toxicity (*Vibrio fischeri* bioassay performed on extracted samples), with toxicity decreasing slightly until 10 Ah L⁻¹, and generally remaining near the initial baseline-toxicity equivalent concentration (TEQ) of the raw concentrate (i.e., ~2 mg L⁻¹). The exception was a high range toxicity measure in the undivided cell (i.e., TEQ = 11 mg L⁻¹ at 2.4 Ah L⁻¹), which rapidly decreased to 4 mg L⁻¹. The discrepancy between the halogenated organic matter and toxicity patterns may be a consequence of volatile and/or polar halogenated by-products formed in oxidation by OH[•] electrogenerated at the anode. The undivided cell exhibited lower energy compared to the divided cell, 0.25 kWh gCOD⁻¹ and 0.34 kWh gCOD⁻¹, respectively, yet it did not demonstrate any improvement regarding by-products formation.

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1. Introduction

For the degradation of organic pollutants, electrochemical oxidation offers an alternative to the existing advanced oxidation processes by eliminating the need to use chemicals to generate highly reactive OH[•]. In electrochemical oxidation, OH[•] is generated by water electrolysis at the anode surface. Recently developed boron-doped diamond (BDD) electrodes have received great

attention [1,2] due to a much wider potential range for O₂ evolution in aqueous electrolytes, which allows efficient formation of OH[•] and other reactive oxygen species [3,4]. BDD electrodes have been investigated for electrochemical oxidation of saline wastewater such as landfill leachate and reverse osmosis concentrate [5–8]. Due to the high content of recalcitrant organic compounds, these streams require an on-site treatment before being discharged into the receiving water bodies [9]. High concentrations of dissolved salts (i.e., chloride ions > 1 g L⁻¹) contained in landfill leachate and reverse osmosis concentrate are attractive for electrochemical processes as they provide a lower internal ohmic resistance, thus reducing the energy demand of the process. However,

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electrochemical oxidation is expected to generate active chlorine species (e.g., Cl_2 , HClO/ClO^-) that may increase the toxicity of the treated stream due to the presence of chlorinated by-products [6,10]. The extent of chlorinated organic compounds formed in electrochemical oxidation depends on the initial characteristics of the stream (e.g., concentrations of chloride ions and organic pollutants) and reactor design and operation (e.g., applied current/potential and cell configuration) [7,11].

A number of studies on electrochemical treatment of municipal wastewater reverse osmosis concentrates have been conducted [6–9,12–14]. These have mainly been focused on the evaluation of the performance of BDD and other anode materials, and effect of current density and chloride ions concentration on the electrochemical oxidation in the undivided (membraneless) electrolytic cell [6–8,12]. Also, a three-dimensional electrode reactor using $\gamma\text{-Al}_2\text{O}_3/\text{Sn-Sb}$ oxide as particle electrodes has been recently developed for the electrochemical treatment of reverse osmosis concentrates [13]. Hurwitz et al. [14] reported an efficient oxidative degradation of organic matter using a hybrid ultraviolet (UV) and electrochemical oxidation process, which also yielded lower amounts of trihalomethanes compared to the stand-alone electrochemical oxidation.

This study investigates the effect of reactor design on the performance of electrochemical oxidation of reverse osmosis concentrate by comparing undivided and membrane-divided electrolytic cell. The undivided cell configuration offers operation at circumneutral pH without the need for pH correction of the treated effluent, and possibly lower energy consumption for reaching specific treatment objectives due to a lower internal resistance. Additionally, in situ cathodic reduction of active chlorine, i.e., HClO/ClO^- species, may lower their bulk concentration and thus decrease the extent of electrochlorination of the organic matter in the undivided cell. Although BDD electrodes have been mainly investigated as anodes, several studies reported excellent performance of cathodically polarised BDD [15,16]. For example, BDD was capable of reducing efficiently bromate to bromide ions [15], and reductively dechlorinating trichloroethylene to acetate and chloride ions, without any intermediate products [16]. Thus, some of the formed organohalogen by-products may also be reduced at the BDD cathode. To the best of our knowledge, comparison of electrochemical oxidation of reverse osmosis concentrate in divided and undivided cell configurations has not been reported in literature. Moreover, the formation of adsorbable organic halogen (AOX) and toxicity response to *Vibrio fischeri* of the oxidised concentrate are also reported, emphasising the need for an integrated approach of combined bioassays and chemical analysis in the assessment of treatment performance.

The treatment efficiency was assessed in terms of chemical oxygen demand (COD) and dissolved organic carbon (DOC) removal. Residual free chlorine and total chlorine were also determined. The formation of halogenated by-products was evaluated based on the measurement of the halogen-specific AOX, i.e., adsorbable organic chlorine (AOCl), bromine (AOBr), and iodine (AOI). Finally, the changes in non-specific, baseline toxicity of the treated stream were evaluated in bioluminescence inhibition test (Microtox) using *V. fischeri*.

2. Experimental

2.1. Reverse osmosis concentrate

The reverse osmosis concentrate was collected in a single sampling batch from the concentrate stream of a reverse osmosis unit process at an inland water recycling plant reclaiming a mixture of secondary-treated effluents. Measured characteristics of the concentrate are detailed in Table 1.

Table 1

Physico-chemical characteristics of the untreated reverse osmosis concentrate used in the current study.

Parameter	Unit	Value ^a
pH		7.72 ± 0.21
Conductivity	mS cm^{-1}	6.01 ± 0.12
COD	$\text{mg O}_2 \text{L}^{-1}$	140 ± 3
DOC	mg C L^{-1}	39 ± 3
Cl^-	mg L^{-1}	1391 ± 74
Br^-	mg L^{-1}	3.06 ± 0.03
I^-	mg L^{-1}	Below detection limit (<0.001)

^a The error values correspond to the standard deviation of duplicate analyses.

2.2. Experimental set-up

The undivided electrochemical cell was comprised of one rectangular Perspex frame (internal dimensions of 20 cm × 5 cm × 2 cm, equal to net active volume (V_{ACT}) of 190 mL), bolted in between two Perspex plates. The divided electrochemical cell was identical to the undivided one, but constructed using two rectangular frames of identical size, with a cation exchange membrane (CMI-7000, Membranes International, U.S.A.) placed between anode and cathode. Two monopolar Si/BDD plate electrodes purchased from Adamant Tech., Switzerland (each 4.8 cm × 8.5 cm × 0.2 cm; active area of 40.8 cm²; 2–3 μm coating thickness of 500 ppm boron) were used as anode and cathode in the undivided cell, with an inter-electrode gap of 1 cm. In the divided cell, the Si/BDD electrode was used as the anode and a stainless steel plate of the same size and shape was used as the cathode. In this case, the reverse osmosis concentrate was treated only in the anodic compartment of the cell. The cathode side in the divided cell was applied only as electron sink, and was expected not to affect the oxidation processes [17]. An Ag/AgCl reference electrode (3 M KCl, 0.210 V vs. standard hydrogen electrode (SHE), Bio-analytical, U.S.A) was used in both cell configurations.

In both undivided and divided cell, batch mode electrochemical oxidation experiments were conducted at constant current of 510 mA (anode potential, $E_{\text{AN}} = +3.9 \text{ V}$ vs. SHE) using a galvanostat (KP07, Bank Elektronik, Germany). Data was recorded every 60 s using an Agilent 34970A (U.S.A.) data acquisition unit. A total volume (V_{TOT}) of 5 L of reverse osmosis concentrate was continuously recirculated through each cell during 120 h at a rate of 120 mL min⁻¹. V_{ACT} is the net active volume of reverse osmosis concentrate electrochemically treated inside the reactor, while V_{TOT} is the total volume of the concentrate recirculated during the batch electrochemical treatment. The ratio of $V_{\text{ACT}}/V_{\text{TOT}}$ in both cell configurations was the same, i.e., 0.038. In the case of the divided cell, 5 L of 0.5 M H_2SO_4 solution was recirculated as catholyte to avoid the formation of a precipitate at the stainless steel cathode, as a result of diffusion of Ca^{2+} ions from the concentrate through the cation exchange membrane and pH increase in the cathodic compartment. The pH in the undivided cell was in the range of 6–7 without pH adjustment, whereas in the divided cell, the pH was maintained at pH 6–7 by an automatic dosing of small aliquots of 3 M NaOH solution. The pH and temperature values were monitored overtime using an Endress + Hauser pH controller (Germany).

2.3. Analytical methods

Samples (110 mL) collected after 0, 24, 48, 72, 96, and 120 h of electrooxidation were filtered using a 0.22 μm Millipore syringe unit. COD, residual free chlorine and total chlorine concentrations were measured directly after sampling. COD was determined using the COD tests range 10–150 mg L⁻¹ (Merck) by a spectrophotometric method. The DOC concentration was analysed using an Analytik Jena multi N/C[®]-series instrument. Residual free

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