Electrochemical oxidation of reverse osmosis concentrate on boron-doped diamond anodes at circumneutral and acidic pH

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**Abstract**

Electrochemical processes have been widely investigated for degrading organic contaminants present in wastewater. This study evaluated the performance of electrochemical oxidation using boron-doped diamond (BDD) electrodes by forming OH\textsuperscript{−} for the treatment of reverse osmosis concentrate (ROC) from secondary-treated wastewater effluents. Since oxidation by OH\textsuperscript{−} and active chlorine species (HClO/ClO\textsubscript{2}/Cl\textsuperscript{2}O\textsubscript{3}) is influenced by pH, the electrochemical oxidation of ROC was evaluated at controlled pH 6–7 and at pH 1–2 (no pH adjustment). A high concentration of chloride ions in the ROC enhanced the oxidation, and 7–11% of Coulombic efficiency for chemical oxygen demand (COD) removal was achieved with 5.2 Ah L\textsuperscript{−1} of specific electrical charge. Complete COD removal was observed after 5.2 and 6.6 Ah L\textsuperscript{−1}, yet the corresponding dissolved organic carbon (DOC) removal was only 48% (at acidic pH) and 59% (at circumneutral pH). Although a higher operating pH seemed to enhance the participation of OH\textsuperscript{−} in oxidation mechanisms, high concentrations of chloride resulted in the formation of significant concentrations of adsorbable organic chlorine (AOCl) after electrochemical oxidation at both pH. While adsorbable organic bromine (AOBr) was degraded at a higher applied electrical charge, a continuous increase in AOCl concentration (up to 0.88 mM) was observed until the end of the experiments (i.e. 10.9 Ah L\textsuperscript{−1}). In addition, total trihalomethanes (tTHMs) and total haloacetic acids (tHAAs) were further degraded with an increase in electrical charge under both pH conditions, to final total concentrations of 1 and 4 mM (tTHMs), and 12 and 22 mM (tHAAs), at acidic and circumneutral pH, respectively. In particular, tHAAs were still an order of magnitude above their initial concentration in ROC after further electrooxidation. Where high chloride concentrations are present, it was found to be necessary to separate chloride from ROC prior to electrochemical oxidation in order to avoid the formation of chlorinated by-products.

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1. Introduction

Recently, there has been an increase in focus on advanced oxidation processes (AOPs) for industrial and domestic wastewater treatment. These rely on the formation of hydroxyl radicals (OH\textsuperscript{−}) to remove organic contaminants. The need to reduce the consumption of energy and chemicals in AOPs, as well as the introduction of novel electrode materials...
such as boron-doped diamond (BDD), have led to increased interest in application of electrochemical oxidation as a chemical-free, robust and versatile process, which is an alternative to classical methods of forming OH· such as Fenton’s reagent or catalysed peroxide (Martínez-Huitle and Ferro, 2006). BDD anodes are classified as non-active anodes (Comninellis, 1994; Zhu et al., 2008), having a weak interaction between the anode surface and electronegated OH·, and thus a high overpotential for O₂ evolution (Panizza, 2010). The oxidation of organic pollutants at BDD electrodes is thought to occur through direct electron transfer at the electrode surface, via OH· and other formed reactive oxygen species (ROS), as well as oxidants (e.g. Cl₂, SΟ₄²⁻) that are electronegated from salts contained in the wastewater (Martínez-Huitle and Ferro, 2006; Zhu et al., 2008). However, direct oxidation mechanisms require a high electrode surface area, and the reaction itself is limited by mass transfer. Thus, direct electrochemical oxidation by electron transfer at the electrode surface is considered to make a minor contribution to the overall bulk electrolysis, especially at high anode potential, at which the formation of ROS, such as OH·, O³, HO₂, O₂ and H₂O₂, is favoured (Zhu et al., 2008).

Electrochemical oxidation using BDD electrodes has been investigated for the remediation of waste streams such as reverse osmosis concentrate (ROC) and landfill leachate, which are difficult to treat by commonly applied methods (Anglada et al., 2011; Perez et al., 2010; Van Hege et al., 2004; Zhou et al., 2011). Direct disposal of these streams with no or limited additional treatment has raised concerns about the potential effects of elevated concentrations of organic contaminants on the receiving water bodies (Khan et al., 2009). High concentrations of chloride ions in ROC and landfill leachate (i.e. >1 g L⁻¹) lower the internal ohmic resistance of the electrolytic cell, making the electrochemical process more energy-efficient. However, chloride ions are efficiently oxidised at the anode to chlorine, which hydrolyses into hypochlorous acid/hypochlorite ion (HClO/ClO⁻), a long-lived oxidant able to diffuse away from the electrode surface into the bulk solution, resulting in electrochlorination of the organic matter. Although BDD electrodes are expected to generate more OH· than conventional mixed-metal oxide (MMO) electrode materials, BDD electrodes are likely to produce OH· and active chlorines (Boudreau et al., 2010). Indeed, formation of undesirable disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), has been reported in electrochemical oxidation of ROC at both BDD (Perez et al., 2010) and MMO (Bagastyo et al., 2011b) anodes. However, to the authors’ best knowledge, the extent of DBPs formation contributed to halogen-specific organic compounds in the case of ROC oxidation has not been reported to date. Furthermore, the contribution of electrogenerated active chlorines and OH/ROS to the electrochemical oxidation of ROC which can be affected by pH is not well studied.

The equilibrium of active chlorine species (i.e. Cl₂/HClO/ ClO⁻), and thus mechanisms of electrochlorination, is affected by the operating pH, with HClO becoming the main species at pH < 7.5. Furthermore, HClO/ClO⁻ and Cl⁻ ions may scavenge OH· radicals and convert them into less reactive inorganic radicals (e.g. ClO., Cl₂, Cl) (De Laat et al., 2004; Gonzalez et al., 2011), whereas the outcome and degree of scavenging also seem to be strongly pH-dependent. For example, several studies have reported that an increase in pH decreased OH· scavenging by chloride ions, leading to improved mineralisation of organic compounds to CO₂ at pH > 6.0 in UV/H₂O₂ and Fenton’s oxidation (De Laat et al., 2004; Liao et al., 2001). Therefore, the operating pH of the bulk liquid can be expected to affect the outcome of electrochemical oxidation, particularly in the presence of high concentrations of chloride ions.

In this study, we evaluated the efficiency of electrochemical oxidation of ROC using a BDD electrode. High anodic current density was applied in order to ensure an anode potential (Ean) above the threshold thermodynamic potential for electrogeneration of OH·, i.e. >2.38 V vs. standard hydrogen electrode (SHE) in 1 M HClO₄ (Kapalka et al., 2009). The experiments were performed at two pH values: pH 1–2 (no pH adjustment) and adjusted pH to 6–7, with the aim of investigating the influence of pH on the competition between ROS and HClO/ClO⁻ and other reactive halogen species (RHS) for the electrochemical oxidation of ROC. The performance of electrochemical oxidation of ROC was evaluated based on the removal of chemical oxygen demand (COD) and dissolved organic carbon (DOC), as well as the generation of halogen-specific adsorbable organic halogen (AOX), namely adsorbable organic chlorine (AOCI), bromine (AOBr) and iodine (AOI), and low molecular weight (MW) DBPs, i.e. THMs and HAAs.

2. Materials and methods

2.1. Reverse osmosis concentrate

The ROC used in the experiments was collected in a single sampling batch from an inland water recycling plant which reclams a mixture of secondary-treated effluents through microfiltration/reverse osmosis membranes after passing pre-treatment processes (Text S1). The characteristics of ROC are given in Table 1.

2.2. Experimental set-up

The bench-scale electrochemical cell was comprised of two rectangular Perspex frames with internal dimensions of...
20 × 5 × 2 cm (net active volume, V_{ACT}: 190 mL), bolted in between two Perspex plates. The anode and cathode cell compartments were separated by a cation exchange membrane (Ultrix CMI-7000, Membranes International, U.S.A). The BDD anode (Si/BDD coating thickness: 2–3 μm; 500 ppm boron; overall thickness: 0.2 cm) was purchased from Adamant Tech., Switzerland, while a stainless steel plate electrode was used as the cathode. The surface area for each electrode was 4.8 × 8.5 cm². The anode–cathode gap was 1 cm.

The electrochemical experiments were conducted in batch mode at room temperature (22 ± 1 °C) and controlled at a constant current of 510 mA (anodic current density, \( J = 12.5 \, \text{mA cm}^{-2} \)) using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, GmbH, Germany). All potentials were measured by placing an Ag/AgCl reference electrode (3 M KCl solution, +0.210 V vs. SHE, Bio-analytical, U.S.A) in the anode compartment close to the BDD electrode surface. Data was recorded every minute using an Agilent 34970A data acquisition unit (Agilent Technologies, U.S.A.). In order to maintain well-mixed conditions and avoid concentration gradients, both anolyte (i.e. total volume, \( V_{TOT} = 5 \, \text{L of ROC} \)) and catholyte (i.e. 0.5 M H₂SO₄ solution, 2 L) were continuously recirculated through the anode and cathode half-cells, respectively, during 96 h at a rate of 120 mL min⁻¹ with vigorous magnetic stirring in each electrolyte vessel. The experiments were performed at two operating pH values: (i) acidic pH (i.e. pH 1–2) where no pH adjustment was applied during electrolysis, and (ii) controlled, circumneutral pH, where aliquots of a 3 M NaOH solution were automatically added by a dosing system to keep the pH in the range of pH 6–7 during electrolysis. The pH and temperature values were monitored using a pH transmitter (CPM 223, Endress + Hauser) with the probe placed in the holding vessel. In the case of controlled pH conditions, a peristaltic pump was connected to the pH transmitter for the automatic dosing (flow rate: 4–5 mL h⁻¹) into the anodic compartment.

In order to determine the effect of pH on chlorine and oxygen evolution at the BDD electrode used in this study, linear sweep voltammetry (LSV) experiments were performed in electrolyte solutions of the same ionic strength (i.e. \( \mu = 0.5 \)) at pH 7 (0.5 M NaCl solution and 0.16 M Na₂SO₄ solution) and at pH ≤ 1 (0.5 M HCl solution + 0.25 M NaNO₃ solution and 0.25 M H₂SO₄ solution).

2.3. Sample preparation and analysis

Subsamples (55 mL) of the oxidised ROC were taken after 0, 4, 8, 16, 24, 36, 48, 60, 72, 84 and 96 h of electrolysis and filtered using a 0.22 μm Millipore syringe unit prior to further analyses. Free available chlorine (FAC) and total chlorine were measured directly with the N,N-diethyl-p-phenylenediamine (DPD) ferrous titrimetric method (APHA, 1998). It is important to emphasise that oxidants other than FAC present in the solution (e.g. H₂O₂, ClO₂, Br₂) may react with DPD in a similar way to chlorine to form a red dye, thus may interfere with the measurement.

The remaining amount of subsample was then quenched by adding a specific volume of 0.24, 0.48, or 0.71 M Na₂SO₄ solution in order to eliminate further reaction of FAC. Quenching agent was added in 120% excess of the molar concentration of FAC, i.e. 1.2 mol of sulphite per mol of HClO, assuming all FAC was in HClO form. The volume of the quenching agent solution added was kept to a minimum of no more than 2 mL of Na₂SO₄ solutions. Analysis of COD, DOC concentration, colour, the concentration of halide ions, specific ultraviolet absorbance (SUVA_{254}), the concentration of THMs (i.e. trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM)), and the concentration of HAs (i.e. monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)) were described in detail in the Supporting Information (Text S2). Those analyses were performed with no pH adjustment (except as stated). Although the UV₅₅₅ absorbance by organic matter may vary at pH < 4 (APHA, 1998), the effect of pH on UV₅₅₅ absorbance measurement has been confirmed to be minimal, i.e. < 5% difference, at pH 2–8.6 (Weishaar et al., 2003).

Halogen-specific AOX was analysed using an analytical method similar to that described in Kristiana et al. (2009). The method involved acidification of the sample to pH 2, followed by adsorption of adsorbable organic compounds (including halogenated organic compounds) onto activated carbon, which was then combusted and the hydrogen halide gases produced were trapped in MilliQ water in an absorber chamber. The dissolved halide ions in the absorber (Cl⁻, Br⁻, and I⁻) were then analysed by on-line ion chromatography (Dionex ICS 3000). These halide ions correspond to the concentrations of halogen-specific AOX, i.e. AOCl, AOBr and AOI, and are expressed in molar concentrations. Calibration of the system was done using trichlorophenol, tribromophenol and iodophenol standards. Duplicate sample analyses were performed, and the obtained data was reported as a mean value with range used as error.

3. Results and discussion

3.1. Voltammetric characterisation of the anodically-polarised BDD electrode

The LSVs of chlorine and oxygen evolution obtained for electrolyte solutions of the same ionic strength at pH 0.5 (0.5 M HCl solution + 0.25 M NaNO₃ solution and 0.25 M H₂SO₄ solution) and pH 7 (NaCl solution and Na₂SO₄ solution) are depicted in Fig. 1. At pH 0.5, the oxygen evolution peak appeared at +1.7 V vs. SHE (curve a: 0.25 M H₂SO₄ solution), while chlorine evolution started at a lower potential, i.e. +1.5 V vs. SHE (curve b: 0.5 M HCl + 0.25 M NaNO₃ solutions). At pH 7, both oxygen and chlorine evolution shifted to lower potentials of +1.5 V and +1.4 V vs. SHE (curve c: 0.16 M Na₂SO₄ solution; and curve d: 0.5 M NaCl solution), respectively. These results confirm that oxygen and chlorine evolution are in competition at both pH 0.5 and pH 7, with acidic pH increasing the difference between their onset potentials to 0.2 V.

If chloride ions are present, their adsorption onto the anode surface hinders the reaction of oxygen evolution, and chloride ions are oxidised to chlorine (Ferro et al., 2000; Scialdone et al., 2009). This competition can be affected by the
concentration of chloride ions (\([\text{Cl}^-]\)) and solution pH. For example, at increased \([\text{Cl}^-]/C_0\), Polcaro et al. (2009) observed a shift in the onset potential of \(\text{Cl}_2\) evolution at a BDD anode to a lower potential than that required for \(\text{O}_2\) evolution. Ferro et al. (2000) investigated the role of pH (0–3.5) in the chlorine evolution reaction on a BDD electrode at a constant ionic strength. They observed that, at pH < 2.5, chlorine evolution was accelerated, while no dependency was noted at pH 2.5–3.5 (Ferro et al., 2000). Indeed, lower pH is expected to favour the chlorine evolution reaction (Scialdone et al., 2009). A shift of oxygen evolution to lower potential with an increase in pH is in agreement with the results obtained by Martínez-Huitle et al. (2008), suggesting that water oxidation is favoured at higher pH, with oxygen evolution generating protons. On the other hand, although the oxidation of \(\text{Cl}^-\) to \(\text{Cl}_2\) does not explicitly involve protons, the lower potential of chlorine evolution at pH 7 than at pH 0.5 is likely a consequence of the availability of \(\text{Cl}^-\) ions (Ferro et al., 2000).

### 3.2 Evolution of free available chlorine and total chlorine during electrochemical oxidation

Halide ions (\([X^-]\)) can be found in ROC at high concentrations (e.g. >1 g L\(^{-1}\)) as they are efficiently rejected during RO filtration (Khan et al., 2009). In this study, the concentration of chloride ions in ROC was 1.39 ± 0.12 g L\(^{-1}\), with \(\text{Br}^-\) and \(\text{I}^-\) ions being three orders of magnitude lower at 1.6 ± 0.4 mg L\(^{-1}\) and 0.5 ± 0.1 mg L\(^{-1}\), respectively (Table 1). Due to the low initial \([\text{Br}^-]\) and \([\text{I}^-]\) vs. \([\text{Cl}^-]\), it was not possible to monitor their depletion during electrooxidation of ROC. BDD anodes have a high overpotential for oxygen evolution, and the oxidation of \(\text{Cl}^-\) is kinetically favoured (Ferro et al., 2000). Thus, high concentrations of active chlorine (i.e. \(\text{HClO}/\text{ClO}^-\)) in the bulk liquid can be expected.

The depletion of chloride ions and the profile of formed chlorine species (FAC and chloramines) measured during electrochemical oxidation of ROC at acidic pH and circumneutral pH conditions are depicted in Fig. 2. Combined chlorine represents inorganic and organic chloramines, and is calculated by subtracting the concentration of FAC from the concentration of total chlorine. The decrease in \([\text{Cl}^-]\) vs. applied charge (\(Q\)) was faster at acidic pH than at circumneutral pH. The calculated oxidation rate of chloride ions following pseudo-first order kinetics from linear regression of duplicate analyses (22 points) at acidic pH was 0.031 ± 0.002 h\(^{-1}\), whereas at circumneutral pH the rate was lower, i.e. 0.0163 ± 0.001 h\(^{-1}\). This indicates that Cl\(^-\) oxidation was favoured at pH 1–2, likely due to the higher difference in the onset potentials for \(\text{Cl}_2\) and \(\text{O}_2\) evolution at the lower pH, as illustrated in the LSVs.

The increase in FAC and total chlorine concentrations was less pronounced at pH 1–2 than at pH 6–7. The measured FAC concentration in acidic conditions reached a maximum at 171 mg L\(^{-1}\) after 3.8 Ah L\(^{-1}\), and then decreased to 24 mg L\(^{-1}\) at the end of the experiment (\(Q = 10.9\) Ah L\(^{-1}\)). In contrast, at circumneutral pH, the highest FAC concentration of 443 mg L\(^{-1}\) was observed after 5.2 Ah L\(^{-1}\), and decreased to 270 mg L\(^{-1}\) after 10.9 Ah L\(^{-1}\). The concentration of chloramines was also higher at circumneutral pH than at acidic pH, i.e. 484 vs.198 mg L\(^{-1}\), respectively. The concentration of FAC measured in the acidic pH experiment was significantly lower than in the circumneutral pH experiment likely due to \(\text{Cl}_2\) stripping into the gas phase from the bulk water under the acidic pH conditions (Deborde and Von Gunten, 2008).

![Linear sweep voltammograms (LSVs) of BDD anode in aqueous solution: (a) 0.25 M H\(_2\)SO\(_4\) solution (pH 0.5), (b) 0.5 M HCl + 0.25 M NaNO\(_3\) solutions (pH 0.5), (c) 0.16 M Na\(_2\)SO\(_4\) solution (pH 7) and (d) 0.5 M NaCl solution (pH 7). Scan rate: 10 mV s\(^{-1}\).](image)

![Depletion of chloride ions and profile of formed chlorine species (FAC and chloramines) measured vs. Q during electrochemical oxidation of ROC at (a) acidic pH and (b) circumneutral pH conditions. Error value is the average deviation of duplicate analyses.](image)
3.3. Performance of electrochemical oxidation

A relatively constant anode potential (EAN) in the range of 3.4–3.7 V vs. SHE was observed during the 96 h of galvanostatic oxidation (I = 510 mA) of ROC in a batch recirculation system at both acidic and circumneutral pH (Fig. S1). Due to the inert properties of the BDD electrode surface for adsorption of OH radicals, O2 evolution during water electrolysis is slow, and thus the anode exhibits very high EAN, e.g. significantly higher than most conventional MMO electrodes.

The removal of COD, DOC, colour and SUVA254 during the electrochemical oxidation of ROC are shown in Fig. 3, normalised to the initial concentrations of each parameter (Table 1). Complete COD removal was obtained at acidic pH after Q = 5.2 Ah L−1 (at J = 12.5 mA cm−2), faster than at circumneutral pH, where complete removal was achieved after 6.6 Ah L−1 (Fig. 3a). The Coulombic efficiency (equation given in Text S3) for complete COD removal at pH 1–2 and pH 6–7 was 11 and 7%, respectively. Previously, complete COD removal in electrochemical oxidation of ROC from water reclamation plant has been observed after 1–2.5 Ah L−1 in an undivided cell under various operating conditions, e.g. current density, recirculation rate and ratio of VACT:VTOT (Perez et al., 2010; Van Hege et al., 2004; Zhou et al., 2011). While the current density and recirculation rate applied in the present study were comparable, the VACT:VTOT ratio was considerably lower than in the aforementioned studies, thus requiring a higher Q to achieve complete COD removal. Faster COD removal observed at acidic pH was likely a consequence of a more intense electrochlorination of organic matter, with Cl2 and HClO being the dominant species. As pH increases from pH 6 upwards, the chemical reactivity of chlorine species decreases, with increasing formation of the less reactive ClO− and decreasing concentrations of HClO (Deborde and Von Gunten, 2008).

It is important to note that although complete removal of COD was observed already at 5.2 (acidic pH) and 6.6 Ah L−1 (circumneutral pH), the corresponding DOC removal was only 48% and 59%, respectively (Fig. 3a). Faster COD than DOC removal indicates the formation of partially oxidised intermediates. At the end of the experiments (i.e. Q = 10.9 Ah L−1), approximately 36% and 32% of the initial DOC remained in the solution at pH 1–2 and pH 6–7, respectively, but this DOC was not able to be oxidised by the potassium dichromate reagent (K2Cr2O7) in the COD analysis. As can be observed in Fig. 3, the removal of DOC was faster at circumneutral pH during the first 6.6 Ah L−1 compared to acidic pH. While the more intense electrochlorination most likely occurring at acidic pH improved the overall oxidation of organic compounds by reactive chloro-species, and thus the COD removal, it did not result in an enhanced mineralisation of the organic matter. Higher mineralisation at BDD anodes has been explained by the existence of a different type of OH−, i.e. weakly adsorbed, quasi-free OH−, accumulated in the vicinity of the electrode surface (Zhu et al., 2008). A complex scenario of oxidation mechanisms can be expected since the participation of OH− in the oxidation of organic matter is lowered when halide ions (mostly Cl−) are present in the bulk (Grebel et al., 2010), particularly at acidic pH. The chloride ions present in ROC act as efficient scavengers of OH− generated at the BDD anode, yielding ClO− species with HClO− and Cl− as intermediates, in a very fast pseudo-equilibrium which depends on the pH and [Cl−] (De Laat and Le, 2006). The distribution of OH−:ClO− is 1:9 when the oxidation takes place at pH < 3, while at higher pH (i.e. pH > 6) the distribution of OH−:HClO− is 90:10 (De Laat et al., 2004). Therefore, less reactive radical and non-radical RHS were likely the predominant species at acidic pH, and although yielding faster COD removal, they were less capable of bond breaking than OH−. In contrast, mineralisation rate seems independent of pH, rapid DOC removal at the beginning of electrolysis at pH 6–7 was likely obtained by a more intense participation of OH− and possibly other oxidants (e.g. peroxodisulfate (S2O82−) and peroxodicarbonate (C2O62−)) in the oxidative degradation of organic matter (Zhu et al., 2008).

The removal of colour in ROC, generally characterised by high MW humic and fulvic acids (Bagastyo et al., 2011b; Motheo and Pinhedo, 2000), was complete after 3.8 and 1.7 Ah L−1 at acidic and circumneutral pH, respectively (Fig. 3b). This suggests the degradation of humic substances, forming intermediates with little UV–vis absorption (Liao et al., 2008). Decolourisation appears to have been slightly faster at circumneutral pH, which could indicate the enhanced removal of colour-causing organic compounds such as humic substances by the participation of OH−.

SUVA254 has been reported to be strongly correlated with percent aromaticity of aquatic organic matter (Weishaar et al., 2003). At circumneutral pH, a gradual decrease in SUVA254 was

Fig. 3 – Removal of (a) COD and DOC, and (b) colour and SUVA254 vs. Q during electrochemical oxidation of ROC at both acidic pH (closed symbols) and circumneutral pH conditions (open symbols). Note: , COD/COD0; Bereaucratic, DOC/DOC0; ▽, colour/colour0; ◆, SUVA254/(SUVA254)0. Error value was lower than 5%.
observed, reaching 70% removal at $Q = 10.9$ Ah L$^{-1}$, and generally following the removal of DOC (Fig. 3b). This indicates that the UV$_{254}$-absorbing functional groups in the DOC were subject to preferential reaction in the system, and likely converted to non UV$_{254}$-absorbing groups. On the other hand, while a significant decrease in SUVA$_{254}$ during the first 1.7 Ah L$^{-1}$ was observed at acidic pH, i.e. 45% removal, the SUVA$_{254}$ then remained fairly constant until 6.6 Ah L$^{-1}$, indicating that the UV$_{254}$ absorbance and the DOC concentration were decreasing in similar amounts. The final SUVA$_{254}$ removal at pH 1 was 60%. The observed removal of SUVA$_{254}$ in both pH conditions shows the overall preferential removal of the UV$_{254}$-absorbing organic matter in electrochemical oxidation of ROC.

3.4. Formation of AOX during electrochemical oxidation

To assess the formation of halogenated by-products during electrochemical oxidation of ROC at acidic and circumneutral operating pH, halogen-specific AOX analyses were performed, i.e. analyses of AOCI, AOBr and AOI. Fig. 4 shows the formation of AOCI, AOBr and AOI during the electrochemical oxidation of ROC. A slightly higher concentration of AOX was formed at the acidic pH, which was characterised by a slower DOC removal. AOCI was a major species contributing to the AOX (>80% of AOX in mM), consistent with the very high [Cl$^-$] in ROC. AOCI increased from the initial 0.02 mM to approximately 0.88 and 0.81 mM at the end of electrolysis at acidic and circumneutral pH, respectively. However, residual FAC was still measured at the end of the experiments (i.e. 25 and 270 mg L$^{-1}$ at pH 1–2 and pH 6–7, respectively). It is possible that prolonging the electrochemical oxidation time beyond the point at which no residual FAC was present would lead to an oxidative degradation of AOCI. Nevertheless, considering the already very high electrical charge applied in this present study, such an operation would be uneconomic. Furthermore, the amount of chlorine incorporated into the organic matter (i.e. 0.81–0.88 mM) comprised only around 3% of the initial concentration of chloride in the ROC (i.e. 39.5 mM). However, considering the remaining concentration of DOC in the electrochemically treated ROC (15 mg L$^{-1}$ at pH 1–2 and 13 mg L$^{-1}$ at pH 6–7) and the molar concentration ratio between the DOC and AOCI (i.e. 1.25:0.88 and 1.08:0.81 at pH 1–2 and pH 6–7, respectively), an increased toxicity of organic matter, due to the presence of (poly)chlorinated by-products, can be expected. Also, AOCI seemed to be similarly formed at both pH despite the lower FAC levels at acidic pH in the final sample. This is consistent with the dominant species of FAC at acidic pH, i.e. Cl$_2$/HClO, being the more reactive than at circumneutral pH, i.e. HClO/ClO$^-$ (Deborde and Von Gunten, 2008).

A far higher proportion of the available [Br$^-$] and [I$^-$] were converted to halogenated products, i.e. ~100% and >50% molar concentrations, respectively, compared to [Cl$^-$] (i.e. 3%). Reasons for this include that electrogenerated HOBr/OBr$^-$ and HOI/OI$^-$ species are usually more reactive than the corresponding chlorine species, especially with phenolic compounds (Gallard et al., 2003), and that while stripping of chloride into the gas phase occurs during electrochemical oxidation, this process is not relevant for the less volatile bromine and iodine species. In addition, brominated organic compounds will be more amenable to oxidation than their chlorinated analogues, which was characterised by weak carbon-bromine bonds (Tang and Tassos, 1997). At acidic pH, the concentration of AOBr increased almost ten times relative to its initial value, i.e. from 0.003 to 0.026 mM after 0.8 Ah L$^{-1}$. The AOBr concentration remained relatively constant until 3.8 Ah L$^{-1}$, before decreasing to 0.015 mM in the final sample. Likewise, at pH 6–7, the highest [AOBr] of 0.024 mM was observed after 3.8 Ah L$^{-1}$, but it was degraded to 0.007 mM at the end of experiment. On the other hand, AOI was only detected in the first two samples at a very low concentration of 0.002 mM.

Several authors have previously reported the formation of persistent AOX during electrolysis of individual solutions of dyes (Costa et al., 2009) and pharmaceuticals (Boudreau et al., 2010) on BDD electrodes and in the presence of Cl$^-$. On the other hand, Rajkumar and Palanivelu (2004) reported an initial increase followed by a gradual decrease of AOX achieved at extended electrolysis time in electrochemical oxidation of three different chloride-containing wastewaters using Ti/TiO$_2$–RuO$_2$–IrO$_2$ anodes. Since a graphite carbon cathode and an undivided cell were used in the study by Rajkumar and Palanivelu (2004), the decrease in AOX may be a consequence of adsorption of the formed AOX onto the cathode, as we have previously observed (Bagastyo et al., 2011a). The use of an undivided cell may be advantageous in terms of lower ohmic resistance, higher bulk pH and possible reduction of the formed FAC and AOX. However, besides reducing the formed chlorine, the desired ROS species will also be consumed at the cathode, diminishing their participation in the indirect oxidation mechanisms. Furthermore, possible reduction of AOX is in competition with hydrogen evolution, and will be diffusion limited (Polcaro et al., 2009), particularly considering that the remaining fraction that is persistent to oxidation even by the COD test kits will likely be comprised of polychlorinated organic compounds. Also, local pH increase at the cathode often leads to its scaling by insoluble species, e.g. Ca and Mg contained in the ROC (Van Hege et al., 2004), and periodic reversal of polarity is then required to remove scaling. This scaling issue would lead to electrode fouling (and increased energy consumption) which may limit their lifetime of application.

Fig. 4 – Halogen-specific AOX profiles vs. Q in electrochemical oxidation of ROC under acidic pH (closed symbols) and circumneutral pH (open symbols) conditions. ○ and □ represent AOCI, △ and ▲ represent AOBr, while ■ and ◆ represent AOI. Error value is the average deviation of duplicate analyses.
3.5. Formation of THMs and HAAs during electrochemical oxidation

To study the formation of individual halogenated organic by-products during electrochemical oxidation, two commonly measured by-product classes, the THMs and HAAs, were analysed. Fig. 5 shows the molar concentrations of total THMs (tTHMs) and total HAAs (tHAAs) after Q = 5.2 and 10.9 Ah L\(^{-1}\) at acidic and circumneutral pH. The measured concentrations of tTHMs and tHAAs in the untreated ROC were 0.9 and 1.2 \(\mu\)mol L\(^{-1}\), respectively, after 5.2 Ah L\(^{-1}\) of supplied charge at acidic pH. At circumneutral pH, higher concentrations of tTHMs and tHAAs were measured for the same applied charge, i.e. 13 and 29 \(\mu\)mol L\(^{-1}\) after 5.2 Ah L\(^{-1}\) of supplied charge, respectively. This is likely a consequence of increased formation of tTHMs and tHAAs at the higher pH by hydrolysis of other DBPs which were not measured in this study, e.g. haloacetonitriles (HANs) and haloacetaldehydes (HAs). At pH 7, HANs undergo hydrolysis to form haloacetamides as intermediates which can then undergo further hydrolysis to form HAAs, while HAs undergo hydrolysis to form haloethanes (Chen, 2011; Yang et al., 2007). The chlorine- and bromine-equivalent concentrations of measured specific THMs and HAAs can be calculated by the following equation:

\[
\sum C(X)_{DBPs} = \frac{[DBPs] \times N}{MW(DBPs)}
\]

where \(C(X)_{DBPs}\) is the chlorine- (\(C(Cl)_{DBPs}\)) or bromine-equivalent (\(C(Br)_{DBPs}\)) molar concentration of halogen (as mmol L\(^{-1}\) Cl or Br) within a given THM or HAA molecule, \([DBPs]\) is the concentration of the THM or HAA molecule (mg L\(^{-1}\)), \(N\) is the number of the particular halogen atom within the THM or HAA molecule, and \(MW(DBPs)\) corresponds to the MW of the given THM or HAA molecule. After Q = 5.2 Ah L\(^{-1}\), the chlorine-equivalent concentrations of the measured DBPs (sum of chlorine-equivalent concentrations of all THMs and HAAs) represented only 16–28% of AOCl, while the bromine-equivalent concentrations of the measured DBPs comprised 8–32% of AOBr, at both pH. This is in accordance with the reported percentage contribution of THMs and HAAs, i.e. 27% and 15%, respectively, to total organic halogen generated in free chlorine disinfection of natural waters at pH 7 (Hua and Reckhow, 2007).

TCM was the dominant species (>70% of tTHMs on a molar basis), followed by BDCM, DBCM, and TBM. Previously, in electrochemical oxidation of landfill leachate at a BDD anode, Anglada et al. (2011) reported the formation and further degradation of THMs and HANs at higher applied electrical charge. Similar observations were made by Perez et al. (2010) for electrooxidation of ROC at a BDD electrode, although the measured tTHMs concentration was significantly lower than the one observed in our study (0.2 mg L\(^{-1}\) after 4.2 Ah L\(^{-1}\) vs. 1.6 mg L\(^{-1}\) after 5.2 Ah L\(^{-1}\), respectively). However, in our experiments, \(V_{ACT-V_{TOT}}\) ratio was lower than that reported in Perez et al. (2010), allowing for a longer reaction time of free chlorine with the organic matter in the external reservoir. Furthermore, polychlorinated HAAs (i.e. TCAA and DCAA) were prominent among the HAAs measured in this study, while brominated HAAs, i.e. BCAA, MBAA and DBAA were detected at lower concentrations (Table S1). After 10.9 Ah L\(^{-1}\), the concentrations of all measured THMs and HAAs were significantly lowered at both pH, indicating further degradation of these DBPs after prolonged electrolysis time. At the end of the oxidation experiments, only 4 and 8% of the measured chlorine-equivalent of the measured DBPs contributed to AOCl, while bromine-equivalent of the measured DBPs comprised 4 and 18% of AOBr, at acidic and circumneutral pH, respectively. Although enhanced removal by volatilisation was possible for both chloro- and bromo-THMs (particularly at acidic pH), the oxidative degradation of brominated compounds is reported to be faster than the chlorinated species due to the lower bond energy of carbon–bromine bonds than carbon–chlorine bonds (Tang and Tassos, 1997).

3.6. Energy consumption

The energy invested at the end of the experiments was exceptionally high, i.e. up to 104 kWh m\(^{-3}\), and yet it did not result in oxidative degradation of the chlorinated by-products formed at acidic and circumneutral pH. Concerning the COD removal, the energy consumed to achieve a complete COD removal was 43 and 50 kWh m\(^{-3}\) (equivalent to 0.29 and 0.34 kWh g COD\(^{-1}\)) at acidic and circumneutral pH,

Fig. 5 – Formation of: (a) THMs and (b) HAAs measured as their total species in initial sample (0 Ah L\(^{-1}\)) and electrooxidised after Q = 5.2 and 10.9 Ah L\(^{-1}\) at both acidic pH (closed bar) and circumneutral pH (open bar) conditions. Insert: Individual THMs measured at Q = 5.2 Ah L\(^{-1}\) at circumneutral pH with the major species following the molar concentration order: TCM > BDCM > DBCM > TBM. Details of individual THMs and HAAs are provided in Table S1 (Supporting information).
respectively. This value is similar to the one previously reported for a complete COD removal during electrooxidation of ROC on BDD electrode using an undivided cell, i.e. 0.20 kWh g COD⁻¹ (Van Hege et al., 2004; Zhou et al., 2011). Nevertheless, it is important to note that although the COD removal was complete, at the same time points in the experiments the remaining organic fraction exhibited a DOC:AOC1 ratio of 1.83:0.37 and 1.44:0.45 at acidic and neutral pH, respectively, suggesting an increased toxicity of the treated effluent.

4. Conclusions

Complete decolourisation and COD removal during BDD oxidation of ROC were achieved at 5.2 and 6.6 Ah L⁻¹ at pH 1–2 and pH 6–7, respectively, corresponding to the energy consumption of 43 and 50 kWh m⁻³, respectively. At these values of applied specific electrical charge, 48% and 59% of the initial DOC was degraded at the acidic and circumneutral pH, respectively. While enhanced participation of Cl₂/HClO initial DOC was degraded at the acidic and circumneutral pH, values of applied specific electrical charge, 48% and 59% of the.

Complete decolourisation and COD removal during BDD oxidation of ROC were achieved at 5.2 and 6.6 Ah L⁻¹ at pH 1–2 and pH 6–7, respectively, corresponding to the energy consumption of 43 and 50 kWh m⁻³, respectively. At these values of applied specific electrical charge, 48% and 59% of the initial DOC was degraded at the acidic and circumneutral pH, respectively. While enhanced participation of Cl₂/HClO species led to a faster oxidation of organic matter at acidic pH, increased contribution of OH⁻ at pH 6–7 was likely responsible for the enhanced mineralisation performance. Prolonged oxidation time lead to a further degradation of the organics, but also to further electrochlorination, increasing the DOC:AOC1 ratio to 1.25:0.88 and 1.08:0.81 at pH 1–2 and pH 6–7, respectively. Varying the pH had no significant impact on the amount of AOCI formed, and AOBr and AOI formation was limited by the initial concentrations of their corresponding halide ions. On the other hand, lower MW halogenated by-products THMs and HAAs were degraded at higher specific electrical charge to final concentrations of 1 and 4 μM (THMs), and 12 and 22 μM (HAAs), at pH 1–2 and pH 6–7, respectively. Electrochemical oxidation in the presence of high chloride ions concentration will lead to the formation of persistent halogenated by-products, irrespective of the operatio

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Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.watres.2012.08.038.

REFERENCES


