



Removal of organic compounds from cooling tower blowdown by electrochemical oxidation: Role of electrodes and operational parameters



Pradip Saha^{a, b, *}, Harry Bruning^a, Thomas V. Wagner^a, Huub H.M. Rijnaarts^a

^a Department of Environmental Technology, Wageningen University and Research, P.O. Box 17, 6700 AA, Wageningen, the Netherlands

^b Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet, 3114, Bangladesh

HIGHLIGHTS

- Electrochemical oxidation to remove organic compounds from cooling tower blowdown.
- Boron-doped diamond anode has higher removal efficiency than mixed-metal oxide anode.
- The applied current density influences the organic compound removal efficiency.
- Electrochemical oxidation results in the partial transformation of organic compounds.
- The formation of toxic chlorinated by-products needs to be prevented.

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ABSTRACT

The reuse of cooling tower blowdown (CTBD) in the cooling tower itself requires CTBD deionization and a pre-treatment before deionization to remove organic compounds (OCs) that induce membrane fouling. This study assesses the potential of electrochemical oxidation (EO) with a boron-doped diamond (BDD) and a Ti/RuO₂ mixed-metal oxide (MMO) anode for CTBD pre-treatment. Also, the influence of the applied current density (j), initial pH, hydrodynamic conditions, and supporting electrolyte on the process performance was evaluated. Results show that COD and TOC removal were 85 and 51%, respectively, with the BDD-anode; however, they were 50 and 12% with MMO-anode at a j -value of 8.7 mA cm⁻² and neutral pH. An increased j -value increased the COD and TOC removal; however, different pHs, hydrodynamic conditions, and the addition of supporting electrolytes had a minor impact on the removal with both anodes. Liquid chromatography-organic carbon detection analysis showed that the OC in CTBD mainly consisted of humic substances (HS). EO with the BDD-anode resulted in 35% HS mineralization, while the rest of the HS were partially oxidized into low molecular weight compounds and building blocks. However, HS mineralization was limited with the MMO-anode. The mineralization and oxidation were accompanied by the formation of organic and inorganic chlorinated species. These species increased the toxicity to *Vibrio fischeri* 20-fold compared to the initially low-toxic CTBD. Thus, EO with a BDD-anode is a promising pre-treatment technology for the removal of OCs before CTBD deionization, but measures to minimize the chlorinated species formation are required before its application.

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1. Introduction

The reuse of discharged cooling tower water in the cooling tower itself can substantially lower the industrial freshwater footprint. This is especially relevant in fresh water-stressed areas where freshwater stress is expected to increase due to climate change and droughts (Wang et al., 2008). In 2015, the United States withdrew 102 km³ of freshwater for the cooling systems of thermal power

* Corresponding author.

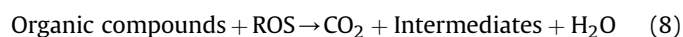
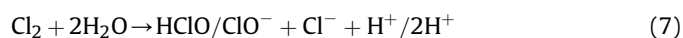
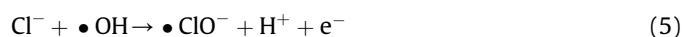
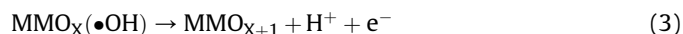
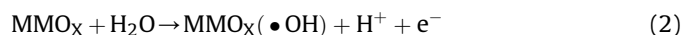
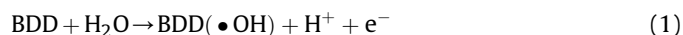
E-mail addresses: pradip.saha@wur.nl, pradip-cep@sust.edu (P. Saha), harry.bruning@wur.nl (H. Bruning), thomas.wagner@wur.nl (T.V. Wagner), huub.rijnaarts@wur.nl (H.H.M. Rijnaarts).

plants (Lohrmann et al., 2019). During the operation of the cooling tower, the concentration of salts and organic compounds (OCs) in the cooling water increases due to evaporation. Increased salt concentrations eventually create operational problems, such as scaling. To prevent operational problems, the concentrated cooling water is discharged regularly as cooling tower blowdown (CTBD) when too high salt concentrations are reached (Nanda et al., 2008; Altman et al., 2012). Subsequently, fresh make-up water needs to be added to the cooling system to compensate for the water loss. To reuse CTBD as make-up water and lower the freshwater footprint of the cooling tower, the deionization of the CTBD is required.

Different membrane technologies for CTBD deionization have been assessed, such as nanofiltration, reverse osmosis (Groot et al., 2015), electrodialysis combined with electrodialysis reversal (Vidic et al., 2009), capacitive deionization (Van Limpt and van der Wal, 2014), and membrane distillation (Koeman-Stein et al., 2015; Kuipers et al., 2015). All these membrane-based deionization technologies encounter fouling through pore-clogging and gel formation as a result of dissolved organic compounds (OCs) that are present in the CTBD (Greenlee et al., 2010; Sweity et al., 2014). Fouling ultimately reduces the deionization efficiency of the membranes. Therefore, a pre-treatment method that removes OCs before membrane deionization would enhance the CTBD deionization efficiency and make the reuse of CTBD in the cooling tower economically more attractive. Several pre-treatment technologies for the removal of OCs from CTBD before membrane deionization have been studied, such as microfiltration (Li et al., 2007), integrated sand filtration/nanofiltration (Wang et al., 2006), coagulation (Davood Abadi Farahani et al., 2016), powdered activated carbon (PAC) (Löwenberg et al., 2015a), ultrafiltration (Zhang et al., 2007, 2008; Zeng et al., 2009) and constructed wetlands (Wagner et al., 2020). The incomplete removal of recalcitrant OCs is a reoccurring issue with the abovementioned pre-treatment technologies. However, during the last decade, electrochemical oxidation (EO) has proven itself as a suitable technology for the removal of recalcitrant OCs from wastewater streams (Moreira et al., 2017; Garcia-Segura et al., 2018; McBeath et al., 2019), such as wastewater from textile industries (Othmani et al., 2020), petrochemical industries (da Silva et al., 2019), pulp and paper mills (Klidi et al., 2018), tanneries (Le Luu et al., 2019), chemical industries (Gomez-Ruiz et al., 2017), municipal secondary effluent (Garcia-Segura et al., 2015), domestic wastewater (Daghrir et al., 2014; Durán et al., 2018) and landfill leachates (Fernandes et al., 2015, 2016; Gautam et al., 2019; Yu et al., 2020). A distinct advantage of EO is that no additional chemicals are required, processes are operated in mild conditions, and processes can easily be automated (Brillas et al., 2009; Sirés et al., 2014; Shin et al., 2019).

In the present study, the application of EO as a CTBD pre-treatment method before CTBD deionization was studied. EO was performed with two different anodes: a Ti/RuO₂ mixed-metal oxide (MMO) anode and a boron-doped diamond (BDD) anode. Both MMO-anodes and BDD-anodes are capable of oxidizing OCs efficiently (Sillanpää and Shestakova, 2017; He et al., 2019; Nidheesh et al., 2019). During the EO of OCs, various mechanisms are responsible for the degradation of OCs. OCs are directly oxidized on the MMO-anode or BDD-anodes surface. In addition, water oxidation results in the formation of hydroxyl radicals ($\bullet\text{OH}$) with both anodes. Furthermore, with the MMO-anode, higher oxidation complexes (MMO_{x+1}) are formed. Additionally, $\bullet\text{OH}$ are capable of forming sulfate radicals and active chlorine species from their corresponding anions present in the water. Moreover, chloride ions can directly be oxidized to chlorine. Chlorine is subsequently converted to hypochlorite. These reactive oxygen species (ROS) can indirectly oxidize the OCs. All the corresponding processes can be

expressed as reactions (1)–(8) (Panizza and Cerisola, 2009; Brito et al., 2015; Farhat et al., 2015; Lan et al., 2017).



In this study, the treatment performance of the MMO-anode and BDD-anode was compared in terms of COD and TOC removal efficiency, average oxidation state (AOS), instantaneous current efficiency (ICE) and energy consumption (EC). Besides, the overall efficiency of EO depends on the applied current density (j), pH, hydrodynamic conditions, and electrolyte composition, and these were varied in the present study to determine their impact on the process efficiency. In addition, the composition of the OCs in CTBD before and after EO-treatment was assessed by liquid chromatography-organic carbon detection (LC-OCD). Furthermore, the formation of adsorbable organic halides (AOX) and chlorinated inorganic species was monitored, and the toxicity of the EO-treated CTBD was assessed because AOX and chlorinated inorganic species are potentially toxic and can accumulate in the environment.

2. Materials and methods

2.1. Chemicals

Potassium ferrocyanide (K₄Fe(CN)₆, ≥98.5%); Potassium ferricyanide (K₃Fe(CN)₆, ≥99%); sulfuric acid (H₂SO₄, 95%); sodium hydroxide (NaOH, ≥99%); sodium nitrate (NaNO₃, 99%); sodium sulfate (Na₂SO₄, ≥99%), sodium chloride (NaCl, ≥99%), calcium chloride (CaCl₂, ≥96%), potassium nitrate (KNO₃, ≥99%), and copper sulfate (CuSO₄, ≥99%) were obtained from Sigma Aldrich (The Netherlands).

2.2. Cooling tower blowdown composition

CTBD was collected from a cooling tower of Dow Benelux BV (Terneuzen, The Netherlands). During normal operation of this cooling tower, H₂SO₄ is dosed for pH-adjustment, Nalco 3DT187, and Nalco 3DT199 are dosed as a corrosion inhibitor, Nalperse 7348 is dosed as bio-dispersant, and NaClO is dosed as a disinfectant (Koeman-Stein et al., 2015). The collected CTBD was stored at 4 °C to minimize microbial activity and growth. Subsequently, the CTBD was used for the experiments without any physical-chemical pre-treatment. The composition of the CTBD is provided in the supplementary info (SI) (Table S1).

2.3. Experimental electrochemical oxidation set-up

EO experiments were performed in batch recirculation mode

using 350 mL CTBD. The electrochemical cell comprises a single flow chambered flat plate reactor assembly with an active electrodes surface area of 22.4 cm² (L: 11.2 cm × W: 2.0 cm) (Fig. S2). The inter-electrode distance was 1.5 cm. A platinum-coated titanium electrode was used as the cathode, and a Ti/RuO₂ mixed-metal oxide (MMO) or boron-doped diamond (BDD) electrode was used as the working anode (Magneto Special Anodes, Schiedam, The Netherlands). A silver/silver chloride (Ag/AgCl) electrode (QM711X/Gel, Prosense, The Netherlands) served as a reference electrode, and it was ionically plugged into the EO cell using Haber-Lugging capillaries filled up with a 1 M potassium nitrate solution. A peristaltic pump was used to circulate the CTBD through the cell at different flow rates. On-line pH, conductivity, and temperature sensors were installed in the set-up. The temperature of the system was maintained at 21–23 °C EO experiments were conducted galvanostatically using an IviumStat.h potentiostat (Ivium Technologies B.V. The Netherlands). The potentiostat was attached in a three-electrode conformation (anode, cathode, and reference electrode). Iviumstat software was used to record and analyses the experimental electrochemical data. The system was polarized at 2.7 mA cm⁻² for 30 min using a 0.1 M sulfuric acid solution prior to the experiments. The mass transfer coefficient of the EO cell was measured by the oxidation and reduction of ferrocyanide and ferricyanide. The detailed protocol of this method is reported in (Cañizares et al., 2006). At a recirculation flow rate of 30 L h⁻¹, the mass transfer coefficient (K_m, m s⁻¹) was 1.7 (±0.06) × 10⁻⁵ m s⁻¹. The limiting current density (I_{lim}) for the CTBD was 3 mA cm⁻², which was calculated according to equation (9) (Panizza and Cerisola, 2009):

$$I_{lim} = 4FAK_mCOD_0 \quad (9)$$

Where, *A* is the surface area of the electrode (m²), *COD*₀ the initial CTBD (mol O₂, m⁻³), and *F* the Faraday's constant (96485 C mol⁻¹).

Na₂SO₄ and NaNO₃ were separately added to the CTBD to assess the effect of the supporting electrolyte on the EO performance. In addition, 96% H₂SO₄ and NaOH solution were added to the CTBD to evaluate the impact of an acidic or basic initial pH on the EO performance.

To determine the COD removal rate and removal efficiency, seven samples of 2 mL were taken for COD analysis during the 3 h EO-treatment. In addition, a 50 mL sample was collected after the 3 h EO-treatment to determine free chlorine (FC, the total concentration of Cl₂ and HOCl/OCl⁻), the TOC concentration, the ionic composition, the composition of the OCs and the toxicity of the treated CTBD.

2.4. Analytical methods

The CTBD OCs concentration was measured as COD using Hach kit LCK-314/LCK-1414 and a Hach DR/3900 spectrophotometer (Hach Lange GmbH, Germany). The degree of OCs mineralization was measured as TOC removal using a TOC-L_{CPH/CPN} analyzer equipped with an ASI-L autosampler (Shimadzu, The Netherlands). The OCs were catalytically oxidized to CO₂ at a temperature of 680 °C, and non-dispersive infrared detection was used to detect the CO₂. Anions were measured with a Dionex ICS-2100 ion chromatography (IC) (Dionex, The Netherlands) connected with a Dionex IonPac AS19 column (4 × 250 mm). A PerkinElmer ICP-OES AVIO 500 plasma atomic emission spectroscopy (ICP) was used to determine the cations. The composition of the OCs in the CTBD samples was analyzed with a size-exclusion liquid chromatography-organic carbon detector (LC-OCD) (Model 8, DOC-Labor, Germany), according to the method described in Ajao et al. (2019). In short, the analyzer was equipped with a non-dispersive

infrared detector together with an organic nitrogen detector (UV 220 nm) and a UV detector (254 nm). Each sample was separated according to their molecular weight into biopolymers, HS, low molecular weight (LMW) acids, and LMW neutrals in the size-exclusion column (Huber et al., 2011; Ajao et al., 2019). The sample was filtered with a 0.45 μm polytetrafluoroethylene filter before analysis. Free chlorine (FC) concentrations were measured by Hach DPD free and total chlorine test reagent and a Hach DR/3900 spectrophotometer (Hach Lange GmbH, Germany). The AOX concentrations were measured with the Hach LCK-390 cuvette test (Hach Lange GmbH, Germany) according to the manufacturer protocol. The acute toxicity of the initial and treated samples was measured by Microtox® toxicity test kits model 500 (Microloan, the Netherlands).

2.5. Data analysis

2.5.1. Performance evaluation

The performance of the EO process was monitored by following the %COD removal, %TOC removal, instantaneous current efficiency (%ICE), and energy consumption (EC in kWh.kg⁻¹ COD). All the corresponding performances are calculated according to the following equations (10)–(13) (Panizza and Cerisola, 2009; Tak et al., 2015; Zou et al., 2017).

$$\%COD\ removal = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100\% \quad (10)$$

$$\%TOC\ removal = \frac{TOC_{in} - TOC_{out}}{TOC_{in}} \times 100\% \quad (11)$$

$$\%ICE = FV_S \left(\frac{COD_{in} - COD_{out}}{mI\Delta t} \right) \times 100\% \quad (12)$$

$$EC = \frac{\Delta E_{cell}It}{(V_S \times \Delta COD)} \quad (13)$$

Where: *COD*_{in} and *COD*_{out} in gO₂ L⁻¹ are respectively the initial and final COD obtained before and after EO treatment. *TOC*_{in} and *TOC*_{out} in g L⁻¹ are respectively, the initial and final TOC obtained before and after EO treatment. *F* is Faraday's constant (96485 C mol⁻¹), *V*_S is electrolyte volume (L), *I* is the applied current (A), *Δt* is the electrolysis time (s), *t* is the electrolysis time (h), *m* = 8 = oxygen equivalent mass (gO₂, eq mol⁻¹) and *ΔE*_{cell} is the average cell voltage (V).

2.5.2. Average oxidation state (AOS)

The change of oxidation state of the organic carbon is expressed as the average oxidation state (AOS) of the organic carbon in the treated CTBD, which was evaluated using equation (14) (Reyes et al., 2006).

$$AOS = 4 \frac{(TOC_{out} - COD_{out})}{TOC_{out}} \quad (14)$$

Where TOC and COD are expressed in molar units, the AOS value varies from +4 to -4. +4 implies the highest oxidation state of the carbon, such as CO₂ or CCl₄. -4 indicates the lowest oxidation stated of the carbon, such as methane.

3. Results and discussion

3.1. Influence of applied current density (j) on OCs oxidation

The COD removal efficiency increased with an increasing applied current density (j) for both anodes (Fig. 1). The applied current density is an important parameter that governs the removal kinetics (Klidi et al., 2018). More ROS are formed at a higher j -value (Panizza and Cerisola, 2009; Brito et al., 2015; Farhat et al., 2015). These ROS indirectly oxidize the COD present in the CTBD. An increase of the j -value with the BDD-anode from 2.3 to 5.5 and 8.7 mA cm⁻² enhanced the COD removal from 45 to 77 and 85%, respectively. (Fig. 1a). With a j -value of 2.3 mA cm⁻², the COD removal was controlled by the formation of ROS, since this j -value is lower than the limiting current density (Kapařka et al., 2008). With a higher j -value, EO of the COD in the CTBD was limited by mass transport, leading to only an 8% increase in COD removal with an increase of the j -value from 5.5 to 8.7 mA cm⁻². In addition to mass transfer limitation, a higher j -value also facilitates undesired oxygen evolution reactions and reduces energy efficiency (Scialdone et al., 2009).

The COD removal over time with the BDD-anode has a two-phase removal profile with a decreasing removal rate after 60 min (Fig. 1a). The simultaneous occurrence of three processes results in this two-phase removal profile: 1) the reaction kinetics of OCs at the surface of the anode; 2) mass-transfer of OCs by diffusion; 3) the transformation of OCs into intermediates with a different reactivity or diffusivity than the parent compound. During the first 60 min, the reaction kinetics are controlled by the •OH formed at the anode surface, and OCs can be supplied at a high enough diffusion rate not to become rate-limiting. After 60 min, the reaction kinetics decrease, possibly by diffusive mass transfer limitation because of the decreased OCs concentration. In addition, the two-phase removal profile might be explained by the production of OC intermediates that are unfavorable to oxidation. Oliveira et al. (2018) reported a similar COD removal profile. In their study, the removal of COD from phenolic wastewaters was faster during the first 0.5 h of treatment, after which the removal slowed down due to mass transfer limitation at the surface of the BDD-anode (Oliveira et al., 2018).

EO with the MMO-anode resulted in incomplete COD removal that is substantially lower than with the BDD-anode for all j values (Fig. 1b). Several competitive processes occur during EO with the

MMO-anode, which could explain the lower COD removal compared to the BDD-anode. Firstly, MO_{x+1} active higher oxidation complexes are formed at the MMO-anode surface, that less efficiently oxidize OCs compared to the •OH produced by the BDD-anode. Also, MO_{x+1} proceeds to oxygen evaluation reactions (Klidi et al., 2018). Secondly, 80, 205, and 310 mg L⁻¹ hypochlorites are formed with a j of 5.5, 8.7, and 14.5 mA cm⁻² with the MMO-anode (Table 3), and hypochlorite has less oxidation potential compared to the •OH formed by the BDD-anode (Wu et al., 2014). Lastly, the low water oxidation overpotential of the MMO-anode (+1.50 V, SHE) compared to the BDD-anode (+2.3 V, SHE) results in a loss of applied energy to undesired water oxidation (Panizza and Cerisola, 2009; Wu et al., 2014).

3.2. Effect of applied current on the performance of the electrochemical oxidation process

During EO, the OCs in CTBD are oxidized and partially mineralized to carbon dioxide. Only part of the applied energy is used for the desired oxidation reactions. Thus, analysis of the TOC removal, the OCs average oxidation state (AOS), instantaneous current efficiency (ICE), and energy consumption allows determining the process efficiency.

An increasing j led to increased removal of TOC with both anodes. A similar phenomenon was observed for COD removal (section 3.1; Table 1). TOC removal represents the complete mineralization of OCs. The higher COD than TOC removal (Table 1) indicates that partial oxidation of OCs occurred, resulting in OC 's with a higher oxidation state (Bilińska et al., 2016). Evaluation of the OCs AOS over time confirms this partial oxidation phenomenon since the AOS-values substantially increased after 180 min EO of CTBD with the BDD-anode and the MMO-anode (Table 1). Most likely, a fraction of the OCs was oxidized into smaller organic molecules, especially organic acids, alcohols and aldehydes, and possibly chlorinated OCs (Oller et al., 2011). Several studies indicated that the breakdown of large molecules into smaller and more oxidized organic intermediates corresponds with higher AOS values (Reyes et al., 2006; Orts et al., 2017).

The ICE declined with increasing j -values with the BDD-anode (Table 1). At a low j -value, most of the applied energy is used for oxidation of the OCs. Higher j -value results in decreasing ICE because more energy is used for the oxidation of water. The ICE was substantially lower with the MMO-anode compared to the BDD-

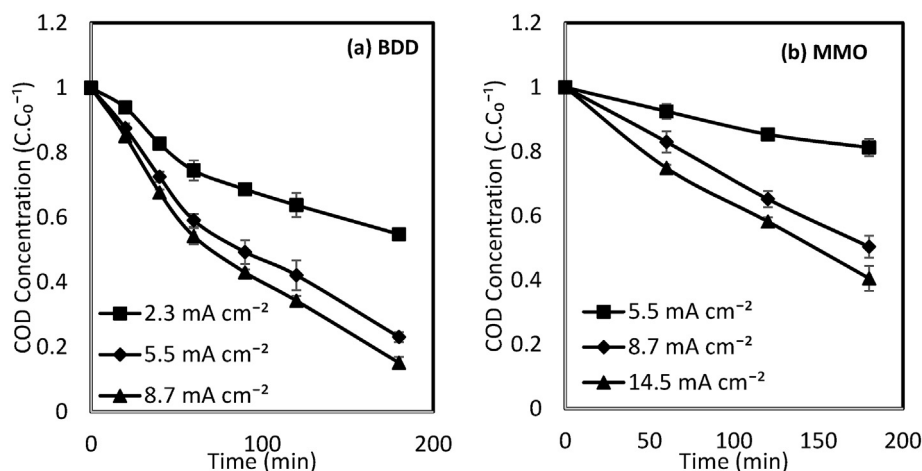


Fig. 1. Influence of applied current density (j) on COD removal with (a) BDD-anode and (b) MMO-anode. Experimental conditions: T = 21–23 °C, Conductivity = 3.7 mS cm⁻¹, pH = 6.9, recirculation flow rate = 30 L h⁻¹.

Table 1

EO performance in terms of COD and TOC removal, average oxidation state (AOS) of the OCs, instantaneous current efficiency (ICE) and energy consumption per kg of COD at different applied current densities (j). Experimental conditions: T = 21–23 °C, conductivity = 3.7 mS cm⁻¹, pH = 6.9, recirculation flow rate = 30 L h⁻¹, treatment time = 3 h.

| Anode | j (mA cm ⁻²) | % COD removal (±) | %TOC removal (±) | AOS ^{a,b} | %ICE ^b | EC (kWh kg ⁻¹ COD) ^b |
|-------|----------------------------|-------------------|------------------|--------------------|-------------------|--|
| BDD | 2.3 | 45 (1) | 39 (1) | +1.5 | 48 | 12 |
| | 5.5 | 77 (2) | 42 (1) | +2.8 | 31 | 24 |
| | 8.7 | 85 (3) | 51 (1) | +3.0 | 20 | 47 |
| MMO | 5.5 | 19 (3) | 9 (1) | +0.9 | 5.0 | 119 |
| | 8.7 | 50 (3) | 12 (0) | +1.5 | 7.0 | 125 |
| | 14.5 | 60 (4) | 15 (2) | +2.3 | 8.0 | 142 |

^a Initial AOS of CTBD: +0.8.

^b AOS, ICE, and EC were calculated based on average COD and TOC value.

anode (Table 1). Consequently, significantly more energy is consumed for the oxidation of a kg of COD with the MMO-anode than with the BDD-anode (Table 1). Hence, the performance efficiency of the BDD-anode is higher than that of the MMO-anode.

3.3. Influence of electrochemical oxidation on the dissolved organic carbon profile

LC-OCD analysis showed that the dissolved organic carbon (DOC) profile of the CTBD changed during EO with the BDD-anode and MMO-anode (Fig. 2). During the EO process, the AOS of the OCs changes, likely because of the conversion of large organic molecules to smaller oxidized organic molecules (section 3.2).

Before EO, the CTBD is composed of 35.1 mg L⁻¹ HS, 1.6 mg L⁻¹ biopolymers, 1.8 mg L⁻¹ low molecular weight (LMW) acids, and 9.8 mg L⁻¹ LMW-neutrals (Fig. 2), which agrees with the earlier described composition of CTBD from the same site (Löwenberg et al., 2015b). EO with the BDD-anode at the highest applied j -value resulted in the removal of HS, while this removal was less apparent with the MMO-anode (Fig. 2). A shoulder appears on the HS peak after EO-treatment with the BDD-anode in the total ion chromatogram of the LC-OCD analysis (Fig. S3). This shoulder indicates the formation of a low molecular weight fraction, building blocks, during the oxidation of HS (Huber et al., 2011). The concentration of the LMW-acids also increased after EO with the BDD-anode. The formation of building blocks and LMW-acids corroborates that HS are partially oxidized and broken down into smaller

fragments, leading to higher COD removal than TOC removal and an increased AOS, as was discussed in sections 3.1 and 3.2.

The ineffective removal of HS with the MMO-anode can be attributed to the less effective oxidation because of the formation of HClO/CIO⁻. HClO/CIO⁻ produced by a SnO₂-Sb₂O₄ (MMO)-anode has shown to indirectly oxidizes HS in sanitary landfill leachate, resulting in 66% COD and 15% DOC removal at a j -value of 30 mA cm⁻² and 8 h of treatment in the presence of 2.5 g L⁻¹ chloride (Fernandes et al., 2016). The low DOC removal compared to the COD removal shows that the MMO-anode is ineffective for the breakdown and mineralization of HS.

3.4. Influence of hydrodynamic conditions on OCs oxidation

Varying the flowrate (linear flow velocity) between 18 L h⁻¹ (0.84 cm s⁻¹), 30 L h⁻¹ (2.8 cm s⁻¹) or 46 L h⁻¹ (4.25 cm s⁻¹) at 8.7 mA cm⁻² for the BDD-anode and 14.5 mA cm⁻² for the MMO-anode did not result in substantial changes in the COD removal efficiency or removal rate (Fig. 3).

Generally, the removal of OCs by EO depends on the dynamics of the flow regime (Scialdone et al., 2009). Approximately 10% variation in the COD removal efficiency was observed for the different flow rates with both anodes. The TOC removal also did not change substantially because of the flow rate variation (Table S2). It was expected that increasing the flow rate would reduce the mass transfer limitation by reducing the diffusion layer thickness and increasing the reaction rate (Scialdone et al., 2009), and in this way

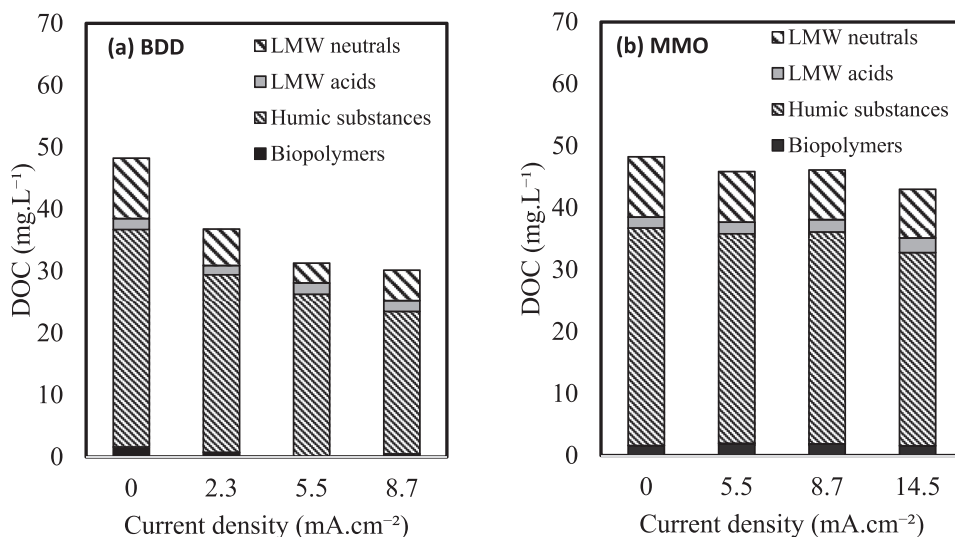


Fig. 2. The DOC-profile of CTBD OCs after EO at different j -values with (a) BDD-anode and (b) MMO-anode. Experimental conditions: T = 21–23 °C, conductivity = 3.7 mS cm⁻¹, pH = 6.9, recirculation flow rate = 30 L h⁻¹, treatment time = 3 h.

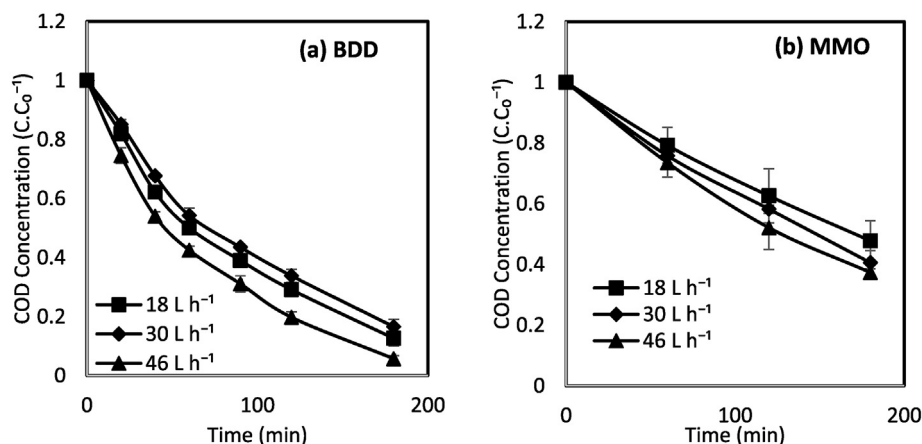


Fig. 3. COD removal at different flowrates with a) BDD-anode and b) MMO-anode. Experimental conditions: $T = 21\text{--}23\text{ }^{\circ}\text{C}$; conductivity = 3.7 mS cm^{-1} ; pH = 6.9; treatment time = 3 h.

improving the COD removal efficiency. The unaffected COD removal efficiency at varying flowrates shows that the COD removal is not only limited by mass transfer and reaction kinetics of the parent OCs, as was discussed in section 3.1 but also by the oxidation rate of the OCs intermediates with the reactive oxidative species formed in the EO system.

3.5. Influence of pH and supporting electrolyte on OCs oxidation

Varying the initial pH between 3.0, 6.9, and 11.5 did not affect the COD and TOC removal efficiency of both anodes (Table 2). EO with the BDD-anode results in the formation of $\cdot\text{OH}$. Their oxidation power is unaffected by different pH values, as was previously shown during the treatment of ferulic acid (Ellouze et al., 2016), paper mill wastewater (Klidi et al., 2018), and sinapinic acid-containing wastewater (Nidheesh and Gandhimathi, 2012a). During EO with the MMO-anode, active chlorine species are responsible for the oxidation of OCs. The pH does influence the formation of active chlorine species. HOCl is the dominating species at an acidic pH and has a higher oxidation potential (1.63 V/SHE) compared to ClO^- (0.89 V/SHE) (Garcia-Segura et al., 2015). Therefore, it was expected that the OCs removal with the MMO-anode would be higher at pH 3 than at pH 11.5. Nevertheless, the COD and TOC removal were comparable at both pHs (Table 2). This was the result of a fast increase of pH 3 to pH 6.5 during the first h of EO with the MMO-anode, which is a similar pH as the initial CTBD pH. Hence, CTBD can be electrochemically treated without adjusting the pH.

The addition of NaNO_3 electrolyte lowered the COD and TOC

removal with the BDD-anode, while these were unaffected by the addition of Na_2SO_4 electrolyte (Table 2). With the MMO-anode, the COD and TOC removal were not affected by either electrolyte (Table 2). Supporting electrolytes enhance the electric conductivity and electron transfer (Nidheesh and Gandhimathi, 2012b). NaNO_3 may increase the surface covering and lower the ROS formation on the BDD-anode surface. In contrast, Na_2SO_4 leads to the formation of strong oxidants, such as sulfate radicals and persulfate, which can improve the removal efficiency. Several researchers indicated that the EO of OCs with a BDD-anode is faster in sulfate electrolyte than in nitrate electrolyte because of the formation of active sulfate species together with $\cdot\text{OH}$ (Sanly et al., 2007; Farhat et al., 2015). The original CTBD contains around 1.1 g L^{-1} sulfate salts, and thus additional sulfate did not improve the process performance. Nevertheless, the supporting electrolyte lowers the EC by reducing the internal resistance of the system (Table 2). The addition of electrolyte increases the CTBD electrical conductivity from 3.4 to 8.0 mS cm^{-1} and decreases the overall cell voltage by lowering the voltage drop (iR drop) (Sillanpää and Shestakova, 2017). Hence, Na_2SO_4 electrolyte can be added during the EO of CTBD to reduce the EC, without affecting the OCs removal efficiency.

3.6. Formation of chlorinated species and their effect on the acute toxicity of CTBD

EO of the chloride-containing CTBD by the BDD-anode and MMO-anode at different j -values resulted in the formation of various organic and inorganic chlorinated species (Table 3). This resulted in an increase in the acute toxicity of the treated CTBD to

Table 2
The effect of different initial pHs and supporting electrolytes on COD and TOC removal, instantaneous current efficiency (ICE) and energy consumption. Experimental conditions: $j = 8.7\text{ mA cm}^{-2}$ (BDD) and 14.5 mA cm^{-2} (MMO), $T = 21\text{--}23\text{ }^{\circ}\text{C}$, conductivity = 3.7 mS cm^{-1} , recirculation flow rate = 30 L h^{-1} , treatment time = 3 h.

| Anode | Parameters | % COD removal (\pm) | % TOC removal (\pm) | % ICE ^a | EC ($\text{kWh kg}^{-1}\text{ COD}$) ^a |
|-------|--------------------------------|-------------------------|-------------------------|--------------------|---|
| BDD | pH = 6.9 (CTBD) | 85 (3) | 51 (1) | 20 | 47 |
| | pH = 3.0 | 88 (1) | 49 (5) | 21 | 42 |
| | pH = 11.5 | 92 (4) | 53 (3) | 22 | 40 |
| | 28 mM Na_2SO_4 | 90 (3) | 50 (3) | 22 | 31 |
| | 48 mM NaNO_3 | 75 (2) | 35 (1) | 19 | 37 |
| MMO | pH = 6.9 (CTBD) | 60 (4) | 15 (2) | 8.0 | 142 |
| | pH = 3.0 | 54 (4) | 20 (2) | 8.7 | 124 |
| | pH = 11.5 | 56 (1) | 17 (1) | 8.9 | 122 |
| | 28 mM Na_2SO_4 | 54 (2) | 20 (1) | 8.8 | 109 |
| | 48 mM NaNO_3 | 51 (3) | 21 (2) | 7.0 | 135 |

^a The ICE and EC were calculated based on average COD value.

Table 3

Chlorinated by-products and bioluminescence inhibition (BI) before and after EO of CTBD with the BDD-anode and MMO-anode at different j -values. Experimental conditions: T = 21–23 °C, conductivity = 3.7 mS cm⁻¹, pH = 6.9, recirculation flow rate = 30 L h⁻¹, treatment time = 3 h.

| | Applied current (mA cm ⁻²) | Cl ⁻ (mg L ⁻¹) | ClO ⁻ (mg L ⁻¹) | ClO ₂ (mg L ⁻¹) | ClO ₃ (mg L ⁻¹) | ClO ₄ (mg L ⁻¹) | AOX (mg Cl ⁻ L ⁻¹) | % BI |
|--------------|--|---------------------------------------|--|--|--|--|---|------|
| Initial CTBD | – | 505 (12) | – | – | – | – | 1.78 | <5 |
| BDD | 2.3 | 400 (9) | 35 (2) | 55 (3) | 15 (1) | 15 (1) | 16 (3) | >80 |
| | 5.5 | 312 (12) | 78 (2) | 192 (1) | 44 (3) | 15 (1) | 15 (1) | >90 |
| | 8.7 | 290 (10) | 152 (6) | 302 (5) | 82 (2) | 17 (1) | 17 (1) | >90 |
| MMO | 5.5 | 426 (3) | 80 (3) | 18 (1) | – | 19 (2) | 19 (2) | >90 |
| | 8.7 | 387 (7) | 205 (5) | 56 (3) | – | 23 (4) | 23 (4) | >90 |
| | 14.5 | 346 (1) | 310 (3) | 109 (4) | – | 20 (3) | 20 (3) | >90 |

Vibrio fischeri, as evidenced by the % bioluminescence inhibition (BI) (Table 3).

•OH formed during EO with the BDD anode may oxidize Cl⁻ to ClO₄⁻ via the (Cl⁻ $\xrightarrow{\bullet\text{OH}}$ ClO₂⁻ $\xrightarrow{\bullet\text{OH}}$ ClO₃⁻ $\xrightarrow{\bullet\text{OH}}$ ClO₄⁻) pathway (Lan et al., 2017). The MMO-anode mainly forms HClO/ClO⁻ during EO, and the absence of •OH leads to less oxidation towards ClO₃⁻. Therefore, less ClO₃⁻ was produced with the MMO-anode compared to the BDD-anode, and no ClO₄⁻ was produced with the MMO-anode (Table 3). However, the AOX production with the MMO-anode was higher than with the BDD-anode (Table 3), due to the chlorination of OCs with the produced HClO/ClO⁻ (section 3.1) (Aquino Neto and De Andrade, 2009; Fields and Fields, 2014).

EO of the CTBD with both anodes significantly enhanced the acute toxicity of the initially non-toxic CTBD to *Vibrio fischeri* (Table 3), likely because of the production of the inorganic and organic chlorinated species. To determine the cause of the toxicity, EO with a synthetic solution without OCs (Table S3) based on the real CTBD (Table S1) was performed. EO-treatment of 3 h with a j -value of 5.5 mA cm⁻² with both anodes resulted in a BI of 80%, indicating that ClO⁻, ClO₃⁻ and ClO₄⁻ were responsible for the increase in BI, and not the production of chlorinated organic by-products (AOX) from the OCs. Another indication that chlorinated organic by-products from the OCs do not contribute to the acute toxicity of the EO-treated CTBD is that despite differences in TOC removal efficiency with different j -values, the toxicity is similar (Table 3). Also, similar AOX production but low ClO₃⁻ and ClO₄⁻ production at the lowest j -value of 2.3 mA cm⁻² with the BDD-anode resulted in the lowest BI (Table 3). A similar increase in toxicity as a result of the production of ClO₃⁻ and ClO₄⁻ was observed by Wang et al. (2016) and García-Espinoza et al. (2018) (Wang et al., 2016; García-Espinoza et al., 2018).

Preventing inorganic chlorinated species evolution is essential for the viability of EO as a pre-treatment technology for CTBD for reuse as make-up water in the cooling tower. The production of hypochlorite (HClO/ClO⁻) is somewhat beneficial since it can act as a disinfectant in the cooling tower system and as a continuous cleaning agent for the membranes in the deionization step (Puspitasari et al., 2010). Han et al. (2012) reported that RO (RE8040-UE) and NF (TFC-SR3) membranes remove 60–90% ClO₄⁻ from water containing a mixture of salts and natural organic matter. Therefore, from an application perspective, inorganic chlorinated species formation and toxicity do not make EO of CTBD an immediate bottleneck, as long as the emission of reactive chlorine and AOX species to the environment is prevented, accumulation in the cooling tower system is carefully monitored and EO is smartly integrated with other CTBD treatment technologies.

4. Conclusions

Cooling tower blowdown (CTBD) needs a pre-treatment that removes recalcitrant organic compounds (OCs) before it can be desalinated and reused in the cooling tower itself. The present

study shows that electrochemical oxidation (EO) is a potential pre-treatment technology to remove OCs from CTBD, especially when employing a boron-doped diamond (BDD) anode. With this anode, 51% of the OCs were mineralized with an applied current density of 8.3 mA cm⁻², while the remaining OCs were partially oxidized. Increasing the applied current density enhanced the OCs removal efficiency, while acidic and basic pHs, different hydrodynamic conditions, and the addition of supporting electrolytes effect on the OCs removal efficiency were limited. The OCs in CTBD mainly consisted of humic substances (HS), and 35% of these humic substances were mineralized after EO-treatment with the BDD-anode. Part of the remaining humic substances were transformed into low-molecular-weight substances and building blocks after EO-treatment with the BDD-anode. The mineralization and transformation of OCs are accompanied by the formation of ClO⁻, ClO₃⁻, ClO₄⁻ and adsorbable organic halides (AOX). As a result of the formation of these products, the toxicity of the initially non-toxic CTBD to *Vibrio fischeri* increased 20-fold after EO-treatment. From an application perspective, the production of chlorinated by-product hypochlorite (ClO⁻) can be advantageous, because it can act as a disinfectant in the cooling tower system. However, toxic by-product formation and accumulation need to be critically monitored when applying EO with the BDD-anode for CTBD-treatment.

Credit author statement

Pradip Saha: Conceptualization, Methodology, Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing. **Thomas V. Wagner:** Conceptualization, Writing - Original Draft, Writing - Review & Editing. **Harry Bruning:** Conceptualization, Supervision, Writing - Original Draft, Writing - Review & Editing. **Huub H.M. Rijnaarts:** Supervision, Writing - Review & Editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- Ajao, V., Millah, S., Gagliano, M.C., Bruning, H., Rijnaarts, H., Temmink, H., 2019. Valorization of glycerol/ethanol-rich wastewater to biofloculants: recovery, properties, and performance. *J. Hazard Mater.* 375, 273–280.
- Altman, S.J., Jensen, R.P., Cappelle, M.A., Sanchez, A.L., Everett, R.L., Anderson, H.L., McGrath, L.K., 2012. Membrane treatment of side-stream cooling tower water for reduction of water usage. *Desalination* 285, 177–183.
- Aquino Neto, S., De Andrade, A.R., 2009. Electrochemical degradation of glyphosate formulations at DSA® anodes in chloride medium: an AOX formation study. *J. Appl. Electrochem.* 39, 1863–1870.
- Bilińska, L., Gmurek, M., Ledakowicz, S., 2016. Comparison between industrial and simulated textile wastewater treatment by AOPs – biodegradability, toxicity and cost assessment. *Chem. Eng. J.* 306, 550–559.
- Brillas, E., Sirés, I., Oturan, M.A., 2009. Electro-fenton process and related electrochemical technologies based on fenton's reaction chemistry. *Chem. Rev.* 109, 6570–6631.
- Brito, C.D.N., De Araújo, D.M., Martínez-Huitle, C.A., Rodrigo, M.A., 2015. Understanding active chlorine species production using boron doped diamond films with lower and higher sp³/sp² ratio. *Electrochim. Commun.* 55, 34–38.
- Cañizares, P., García-Gómez, J., Fernández de Marcos, I., Rodrigo, M.A., Lobato, J., 2006. Measurement of mass-transfer coefficients by an electrochemical technique. *J. Chem. Educ.* 83, 1204–1207.
- da Silva, S., Venzke, C.D., Welter, J.B., Schneider, D.E., Ferreira, J.Z., Rodrigues, M.A.S., Bernardes, A.M., 2019. Electrooxidation using Nb/BDD as post-treatment of a reverse osmosis concentrate in the petrochemical industry. *Int. J. Environ. Res. Publ. Health* 16.
- Daghrir, R., Drogui, P., Tshibangu, J., 2014. Efficient treatment of domestic wastewater by electrochemical oxidation process using bored doped diamond anode. *Separ. Purif. Technol.* 131, 79–83.
- Davood Abadi Farahani, M.H., Borghei, S.M., Vatanpour, V., 2016. Recovery of cooling tower blowdown water for reuse: the investigation of different types of pre-treatment prior nanofiltration and reverse osmosis. *J. Water Process Eng.* 10, 188–199.
- Durán, F.E., de Araújo, D.M., do Nascimento Brito, C., Santos, E.V., Ganiyu, S.O., Martínez-Huitle, C.A., 2018. Electrochemical technology for the treatment of real washing machine effluent at pre-pilot plant scale by using active and non-active anodes. *J. Electroanal. Chem.* 818, 216–222.
- Ellouze, S., Panizza, M., Barbucci, A., Cerisola, G., Mhiri, T., Elaoud, S.C., 2016. Ferulic acid treatment by electrochemical oxidation using a BDD anode. *J. Taiwan Inst. Chem. Eng.* 59, 132–137.
- Farhat, A., Keller, J., Tait, S., Radjenovic, J., 2015. Removal of persistent organic contaminants by electrochemically activated sulfate. *Environ. Sci. Technol.* 49, 14326–14333.
- Fernandes, A., Pacheco, M.J., Ciriaco, L., Lopes, A., 2015. Review on the electrochemical processes for the treatment of sanitary landfill leachates: present and future. *Appl. Catal. B Environ.* 176–177, 183–200.
- Fernandes, A., Santos, D., Pacheco, M.J., Ciriaco, L., Lopes, A., 2016. Electrochemical oxidation of humic acid and sanitary landfill leachate: influence of anode material, chloride concentration and current density. *Sci. Total Environ.* 541, 282–291.
- Fields, E., Fields, S.E., 2014. Electrochemical treatment of reverse osmosis concentrates. In: Kreysa, Gerhard, Ken-ichiro Ota, R.F.S. (Eds.), *Encyclopedia of Applied Electrochemistry*, pp. 644–650.
- García-Espinoza, J.D., Mijaylova-Nacheva, P., Avilés-Flores, M., 2018. Electrochemical carbamazepine degradation: effect of the generated active chlorine, transformation pathways and toxicity. *Chemosphere* 192, 142–151.
- García-Segura, S., Keller, J., Brillas, E., Radjenovic, J., 2015. Removal of organic contaminants from secondary effluent by anodic oxidation with a boron-doped diamond anode as tertiary treatment. *J. Hazard Mater.* 283, 551–557.
- García-Segura, S., Ocon, J.D., Chong, M.N., 2018. Electrochemical oxidation remediation of real wastewater effluents — a review. *Process Saf. Environ. Protect.* 113, 48–67.
- Gautam, P., Kumar, S., Lokhandwala, S., 2019. Advanced oxidation processes for treatment of leachate from hazardous waste landfill: a critical review. *J. Clean. Prod.* 237.
- Gomez-Ruiz, B., Gómez-Lavín, S., Diban, N., Boiteux, V., Colin, A., Dauchy, X., Urriaga, A., 2017. Boron doped diamond electrooxidation of 6:2 fluorotelomers and perfluorocarboxylic acids. Application to industrial wastewaters treatment. *J. Electroanal. Chem.* 798, 51–57.
- Greenlee, L.F., Testa, F., Lawler, D.F., Freeman, B.D., Moulin, P., 2010. Effect of antiscalants on precipitation of an RO concentrate: metals precipitated and particle characteristics for several water compositions. *Water Res.* 44, 2672–2684.
- Groot, C.K., Van Den Broek, W.B.P., Loewenberg, J., Koeman-Stein, N., Heidekamp, M., De Schepper, W., 2015. Mild desalination of various raw water streams. *Water Sci. Technol.* 72, 371–376.
- Han, J., Kong, C., Heo, J., Yoon, Y., Lee, H., Her, N., 2012. Removal of perchlorate using reverse osmosis and nanofiltration membranes. *Environ. Eng. Res.* 17, 185–190.
- He, Y., Lin, H., Guo, Z., Zhang, W., Li, H., Huang, W., 2019. Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants. *Separ. Purif. Technol.* 212, 802–821.
- Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). *Water Res.* 45, 879–885.
- Kapaika, A., Fóti, G., Comninellis, C., 2008. Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment. *J. Appl. Electrochem.* 38, 7–16.
- Klidi, N., Clematis, D., Delucchi, M., Gadri, A., Ammar, S., Panizza, M., 2018. Applicability of electrochemical methods to paper mill wastewater for reuse. Anodic oxidation with BDD and TiRuSnO₂ anodes. *J. Electroanal. Chem.* 815, 16–23.
- Koeman-Stein, N.E., Creusen, R.J.M., Zijlstra, M., Groot, C.K., Van Den Broek, W.B.P., 2015. Membrane distillation of industrial cooling tower blowdown water. *Water Resour. Ind.* 14, 11–17.
- Kuipers, N., van Leerdam, R., van Medevoort, J., van Tongeren, W., Verhasselt, B., Verelst, L., Vermeersch, M., Corbisier, D., 2015. Techno-economic assessment of boiler feed water production by membrane distillation with reuse of thermal waste energy from cooling water. *Desalin. Water Treat.* 55, 3506–3518.
- Lan, Y., Coetsier, C., Causserand, C., Groenen Serrano, K., 2017. On the role of salts for the treatment of wastewaters containing pharmaceuticals by electrochemical oxidation using a boron doped diamond anode. *Electrochim. Acta* 231, 309–318.
- Le Luu, T., Stephane, D.D.F., Minh, N.H., Canh, N.D., Thanh, B.X., 2019. Electrochemical oxidation as a post treatment for biologically tannery wastewater in batch reactor. *Water Sci. Technol.* 80, 1326–1337.
- Li, J., Xu, Z.Y., An, H.G., Liu, L.Q., 2007. Study of using microfiltration and reverse osmosis membrane technologies for reclaiming cooling water in the power industry. *Water Environ. Res.* 79, 753–758.
- Lohrmann, A., Farfan, J., Caldera, U., Lohrmann, C., Breyer, C., 2019. Global scenarios for significant water use reduction in thermal power plants based on cooling water demand estimation using satellite imagery. *Nat. Energy* 4, 1040–1048.
- Löwenberg, J., Baum, J.A., Zimmermann, Y.S., Groot, C., van den Broek, W., Wintgens, T., 2015a. Comparison of pre-treatment technologies towards improving reverse osmosis desalination of cooling tower blow down. *Desalination* 357, 140–149.
- Löwenberg, J., Baum, J.A., Zimmermann, Y.S., Groot, C., van den Broek, W., Wintgens, T., 2015b. Comparison of pre-treatment technologies towards improving reverse osmosis desalination of cooling tower blow down. *Desalination* 357, 140–149.
- McBeath, S.T., Wilkinson, D.P., Graham, N.J.D., 2019. Application of boron-doped diamond electrodes for the anodic oxidation of pesticide micropollutants in a water treatment process: a critical review. *Environ. Sci. Water Res. Technol.* 5, 2090–2107.
- Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P., 2017. Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Appl. Catal. B Environ.* 202, 217–261.
- Nanda, D., Tung, K.L., Hsiung, C.C., Chuang, C.J., Ruan, R.C., Chiang, Y.C., Chen, C.S., Wu, T.H., 2008. Effect of solution chemistry on water softening using charged nanofiltration membranes. *Desalination* 234, 344–353.
- Nidheesh, P.V., Gandhimathi, R., 2012a. Trends in electro-Fenton process for water and wastewater treatment: an overview. *Desalination* 299, 1–15.
- Nidheesh, P.V., Gandhimathi, R., 2012b. Trends in electro-Fenton process for water and wastewater treatment: an overview. *Desalination* 299, 1–15.
- Nidheesh, P.V., Divyapriya, G., Oturan, N., Trelu, C., Oturan, M.A., 2019. Environmental applications of boron-doped diamond electrodes: 1. Applications in water and wastewater treatment. *ChemElectroChem* 6, 2124–2142.
- Oliveira, E.M.S., Silva, F.R., Morais, C.C.O., Oliveira, T.M.B.F., Martínez-Huitle, C.A., Motheo, A.J., Albuquerque, C.C., Castro, S.S.L., 2018. Performance of (in)active anodic materials for the electrooxidation of phenolic wastewaters from cashew-nut processing industry. *Chemosphere* 201, 740–748.
- Oller, I., Malato, S., Sánchez-pérez, J.A., 2011. Combination of advanced oxidation processes and biological treatments for wastewater decontamination — a review. *Sci. Total Environ.* 409, 4141–4166.
- Orts, F., del Río, A.I., Molina, J., Bonastre, J., Cases, F., 2017. Electrochemical treatment of real textile wastewater: trichromy Procion HEXL®. *J. Electroanal. Chem.* 808, 387–394.
- Othmani, A., Kesraoui, A., Akrou, H., Elaissoui, I., Seffen, M., 2020. Coupling anodic oxidation, biosorption and alternating current as alternative for wastewater purification. *Chemosphere* 249, 126480.
- Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic pollutants. *Chem. Rev.* 109, 6541–6569.
- Puspitasari, V., Granville, A., Le-Clech, P., Chen, V., 2010. Cleaning and ageing effect of sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane. *Separ. Purif. Technol.* 72, 301–308.
- Reyes, C., Fernández, J., Freer, J., Mondaca, M.A., Zaror, C., Malato, S., Mansilla, H.D., 2006. Degradation and inactivation of tetracycline by TiO₂ 2 photocatalysis. *J. Photochem. Photobiol. Chem.* 184, 141–146.
- Sanly, M., Lim, K.C., Amal, R., Fabris, R., Chow, C., Drikas, M., 2007. A study on the removal of humic acid using advanced oxidation processes. *Separ. Sci. Technol.* 42, 1391–1404.
- Sialdone, O., Randazzo, S., Galia, A., Silvestri, G., 2009. Electrochemical oxidation of

- organics in water: role of operative parameters in the absence and in the presence of NaCl. *Water Res.* 43, 2260–2272.
- Shin, Y.U., Yoo, H.Y., Ahn, Y.Y., Kim, M.S., Lee, K., Yu, S., Lee, C., Cho, K., Kim, H.I., Lee, J., 2019. Electrochemical oxidation of organics in sulfate solutions on boron-doped diamond electrode: multiple pathways for sulfate radical generation. *Appl. Catal. B Environ.* 254, 156–165.
- Sillanpää, M., Shestakova, M., 2017. Introduction. In: *Electrochemical Water Treatment Methods: Fundamentals, Methods and Full Scale Applications*. Matthew Deans, pp. 1–46.
- Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M., 2014. Electrochemical advanced oxidation processes: today and tomorrow. A review. *Environ. Sci. Pollut. Res.* 21, 8336–8367.
- Sweity, A., Ronen, Z., Herzberg, M., 2014. Induced organic fouling with antiscalants in seawater desalination. *Desalination* 352, 158–165.
- Tak, B.-y., Tak, B.-s., Kim, Y.-j., Park, Y.-j., Yoon, Y.-h., Min, G.-h., 2015. Optimization of color and COD removal from livestock wastewater by electrocoagulation process: application of Box–Behnken design (BBD). *J. Ind. Eng. Chem.* 28, 307–315.
- Van Limpt, B., van der Wal, A., 2014. Water and chemical savings in cooling towers by using membrane capacitive deionization. *Desalination* 342, 148–155.
- Vidic, R., Dzombak, D., Hsieh, M.-K., Li, H., Chien, S.-H., Feng, Y., Chowdhury, I., Monnell, J., 2009. Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-Based Thermoelectric Power Plants. University of Pittsburgh, pp. 8–11.
- Wagner, T.V., Parsons, J.R., Rijnaarts, H.H.M., de Voogt, P., Langenhoff, A.A.M., 2020. Benzotriazole removal mechanisms in pilot-scale constructed wetlands treating cooling tower water. *J. Hazard Mater.* 384.
- Wang, Z., Fan, Z., Xie, L., Wang, S., 2006. Study of integrated membrane systems for the treatment of wastewater from cooling towers. *Desalination* 191, 117–124.
- Wang, J., Qu, D., Tie, M., Ren, H., Peng, X., Luan, Z., 2008. Effect of coagulation pretreatment on membrane distillation process for desalination of recirculating cooling water. *Separ. Purif. Technol.* 64, 108–115.
- Wang, W.L., Wu, Q.Y., Huang, N., Wang, T., Hu, H.Y., 2016. Synergistic effect between UV and chlorine (UV/chlorine) on the degradation of carbamazepine: influence factors and radical species. *Water Res.* 98, 190–198.
- Wu, W., Huang, Z., Lim, T., 2014. General Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. *Appl. Catal. Gen.* 480, 58–78.
- Yu, D., Cui, J., Li, X., Zhang, H., Pei, Y., 2020. Electrochemical treatment of organic pollutants in landfill leachate using a three-dimensional electrode system. *Chemosphere* 243, 125438.
- Zeng, H., Zhang, J., Ye, C., 2009. Comparison of an ultrafiltration membrane fed with raw seawater, coagulated seawater and cooling tower blowdown. *Desalination* 244, 199–207.
- Zhang, J., Chen, L., Zeng, H., Yan, X., Song, X., Yang, H., Ye, C., 2007. Pilot testing of outside-in MF and UF modules used for cooling tower blowdown pre-treatment of power plants. *Desalination* 214, 287–298.
- Zhang, J., Zeng, H., Ye, C., Chen, L., Yan, X., 2008. Pilot test of UF pretreatment prior to RO for cooling tower blowdown reuse of power plant. *Desalination* 222, 9–16.
- Zou, J., Peng, X., Li, M., Xiong, Y., Wang, Bing, Dong, F., Wang, Bin, 2017. Electrochemical oxidation of COD from real textile wastewaters: kinetic study and energy consumption. *Chemosphere* 171, 332–338.