



## Cooling tower water treatment using a combination of electrochemical oxidation and constructed wetlands



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### ABSTRACT

A substantial part of the freshwater used in the industry is consumed in cooling towers. Cooling towers discharge saline cooling tower blowdown (CTBD), and the reuse of CTBD in the cooling tower can lower the industrial freshwater footprint. This reuse requires CTBD desalination and a pre-treatment that removes organic chemicals before physico-chemical desalination technologies to be applied efficiently. In the present study, the pre-treatment of CTBD by a combination of electrochemical oxidation (EO) with a boron-doped diamond (BDD) or mixed-metal oxide (MMO) anode and a vertical flow constructed wetland (VFCW) was assessed in both possible configurations. The integrated VFCW-EO systems removed more organic chemicals, such as COD, TOC, and the corrosion inhibitor benzotriazole than the EO-VFCW systems. However, the EO resulted in highly toxic effluent to *Vibrio fischeri* and the plants in the VFCW. This toxicity was the result of the production of unwanted chlorinated organic compounds and  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  by both the BDD- and MMO-anode during EO. These toxic EO by-products were removed substantially in the VFCW during EO-VFCW treatment but did impact the removal efficiency and viability of the VFCW. Moreover, significant water loss was observed in the VFCW due to evapotranspiration. In conclusion, the negative impact of EO effluent on the VFCW and evapotranspiration of the VFCW should be considered during application.

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### 1. Introduction

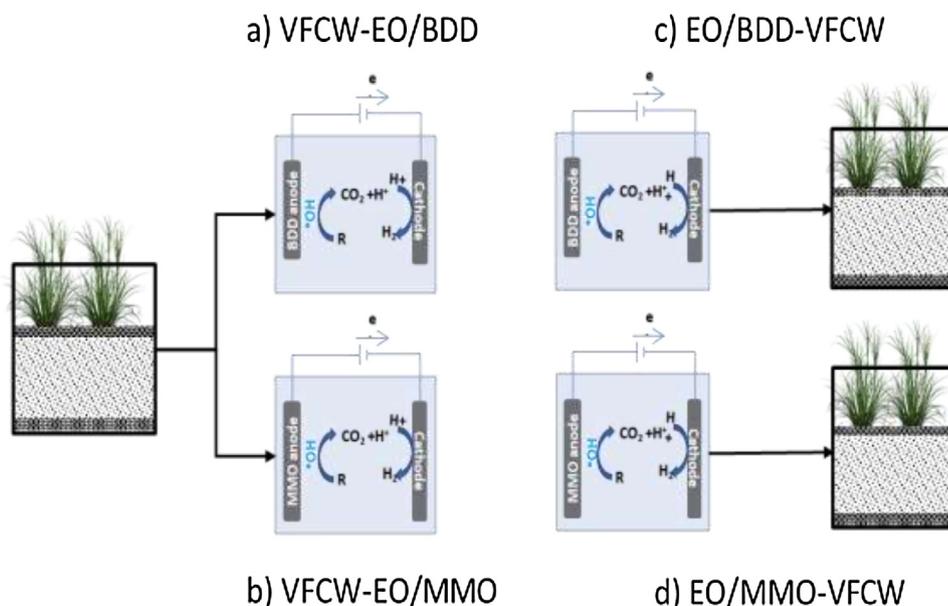
The reuse of discharged cooling tower water in the industry itself lowers the industrial freshwater footprint and alleviates the pressure on natural freshwater resources. Approximately 25 % of the worldwide freshwater withdrawal is used for industrial processes (FAO, 2016), and approximately 40–60 % of the water used in refineries is consumed in cooling towers (dos Santos et al., 2015d). Due to evaporation in the cooling tower, the concentration of salts in the cooling tower water increases. After a salt concentration threshold is reached, cooling tower water is discharged as so-called cooling tower blowdown (CTBD) and replace that with fresh water.

The reuse of this CTBD in the cooling tower itself could allow the industries to reduce their freshwater consumption (Altman et al., 2012; Koeman-Stein et al., 2016).

CTBD mainly contains salts and organic compounds (OCs). The primary sources of OCs in the CTBD are conditioning chemicals, such as benzotriazole, added to the cooling tower water during operation (Koeman-Stein et al., 2016) and humic substances originating from ground water and surface water that are used to compensate for the discharged CTBD (Fateh et al., 2020). The salts result in a CTBD electrical conductivity of approximately 1.5–4.0 mS/cm, and this should be lower than 1.0 mS/cm to enable the reuse of CTBD in the cooling tower (Löwenberg et al., 2015; Davood Abadi Farahani et al., 2016; Bisselink et al., 2016). Hence, desalination is required before reuse of the CTBD in the cooling tower. Several mild physico-chemical desalination technologies for CTBD-treatment have been studied, such as nano-filtration, reverse osmosis, membrane distillation and electro dialysis (Greenlee et al., 2010; Sweity et al., 2014; Löwenberg et al., 2015; Groot et al., 2015; Koeman-Stein et al., 2016). These studies reported that the performance of physico-chemical desalination technologies was hampered due to

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**Fig. 1.** Treatment scenarios for cooling tower blowdown. a) Vertical-flow constructed wetland (VFCW) followed by electrochemical oxidation (EO) by boron doped diamond (BDD)-anode; b) VFCW followed by EO by mixed-metal oxide (MMO)-anode; c) EO by BDD-anode followed by VFCW; d) EO by MMO-anode followed by VFCW.

too high concentrations of OCs in the CTBD. For instance, the OCs create fouling on the nano-filtration or reverse osmosis membranes and scaling on the electrode surface of the electro dialysis reversal system (Greenlee et al., 2010; Sweity et al., 2014). Therefore, a pre-treatment that removes OCs before physico-chemical desalination is required to improve the performance and lifetime of these technologies.

Various pre-treatment methods were studied for the removal of OCs from CTBD before physico-chemical desalination, such as powdered activated carbon, sand filtration, coagulation, ultrafiltration, and biologically active carbon (Löwenberg and Wintgens, 2017; Pramanik et al., 2017). Recently, constructed wetlands (CWs) have been proposed as an attractive alternative pre-treatment method (Wagner et al., 2018, 2020a). CWs are man-made wetlands systems in which various biological, physical, and chemical removal mechanisms function simultaneously to remove compounds from wastewater (Garcia et al., 2010). In addition to the removal of compounds, CWs offer additional benefits: providing the storage of large volumes of treated CTBD that can be used during periods of droughts, increasing the local biodiversity, lowering operation, and maintenance costs. However, various factors limit the application of CWs for CTBD treatment. For instance, CWs are not able to remove some compounds that are recalcitrant to biodegradation and do not adsorb to the CW substrate. Also, OCs in CTBD can cause toxic effects on the microbial communities that are responsible for the degradation of OCs in the CW. For instance, commonly used biocides glutaraldehyde and DBNPA in concentrations that are relevant for cooling tower application can inhibit the biodegradation of OCs by CW microorganisms (Wagner et al., 2020b). Therefore, an additional treatment step combined with CW treatment is necessary for the complete removal of OCs from CTBD before physico-chemical desalination.

Combined biological and chemical treatment systems are a promising option for industrial wastewater, which is not susceptible to a single treatment (Comninellis et al., 2008). Among chemical treatments, electrochemical oxidation (EO) is of interest because of its versatility, controllability, and enhanced removal efficiency for recalcitrant and toxic OCs (Anglada et al., 2009). During EO, electrical energy is applied to form hydroxyl radicals and reactive chlorine species on an anode surface, that can subsequently oxi-

dise OCs (Lan et al., 2017). EO by boron-doped diamond (BDD) and mixed-metal oxide (MMO) anodes is effective for the removal of humic substances (Fernandes et al., 2016) and biocides (Skoumal et al., 2008). The integration of CWs with EO has successfully been applied for the treatment of olive pomace leachate (Grafias et al., 2010), olive washing wastewater (Tatoulis et al., 2017), blackwater (Talekar et al., 2018) and surface water (Wang et al., 2014). However, several researchers reported that a substantial amount of organic halides (AOX), chlorite, and perchlorates are formed during EO of chloride-containing wastewaters (Del Moro et al., 2016; Farhat et al., 2017; Lan et al., 2017). These organic and inorganic chlorinated compounds may hamper the pre-treatment efficiency of CTBD.

In the present study, we assessed the effectiveness of a hybrid system combining EO with a vertical-flow CW system (VFCW) and vice versa for the removal of OCs from CTBD. The performance of two anodes was assessed: a BDD- and an MMO-anode. The process performance was determined according to the COD and TOC removals in the standalone EO- and VFCW systems and combined EO-VFCW and VFCW-EO systems. Benzotriazole, which was already present in the CTBD, was used in both systems as a model compound for the recalcitrant OCs fraction. Furthermore, CTBD contains chloride, and therefore the production of organic and inorganic chlorinated compounds may have an adverse effect on the CTBD pre-treatment efficiency of CWs. Therefore, the concentrations of AOX, chlorite, and perchlorate were monitored. Additionally, micro-toxicity tests were carried out using *Vibrio fischeri* to assess the toxicity of effluents of the different treatments.

## 2. Materials and methods

### 2.1. Chemicals

H<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>, methanol, and acetic acid were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). K<sub>2</sub>PO<sub>4</sub>, CaCl<sub>2</sub>·2H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, and urea were obtained from Merck KGaA (Darmstadt, Germany). NaCl was obtained from VWR chemicals (Leuven, Belgium).

## 2.2. Treatment scenarios

Two different scenarios were used to evaluate and compare the performance of the standalone and combined systems:

Scenario 1: VFCW treatment followed by EO with two different anodes (VFCW-EO) (Fig. 1a and b).

Scenario 2: EO with two different anodes, followed by VFCW treatment (EO-VFCW) (Fig. 1c and d).

EO was performed with either a ruthenium oxide – mixed metal oxide (MMO) or boron-doped diamond (BDD) electrode as the anode; hence the combined systems will be referred to as VFCW-EO/BDD, VFCW-EO/MMO, EO/BDD-VFCW, and EO/MMO-VFCW.

## 2.3. Electrochemical oxidation experiments

The EO experiments were conducted in an undivided flat plate reactor with a 22.4 cm<sup>2</sup> (11.2 cm × 2.0 cm) electrode surface area. A MMO- or BDD-electrode was used as the anode. A platinum-coated titanium- (Pt) electrode was employed as the cathode. Both the anodes and the cathode were provided by Magneto Special Anodes BV (Schiedam, The Netherlands). The distance between the anode and cathode was 1.5 cm. A peristaltic pump was used to recirculate the CTBD in the cell at a flow rate of 10 mL/sec. Based on a previous study of our research group (Saha et al., 2020), all EO experiments were carried out with a current density of 5.5 mA/cm<sup>2</sup> in the EO/BDD cell and 8.7 mA/cm<sup>2</sup> in the EO/MMO cell for 3 h. Before the EO experiment, the system was anodically polarised for 30 min at 2.7 mA/cm<sup>2</sup> using a 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. All experiments were carried out at room temperature and without any additional supporting electrolyte. Original CTBD and day-3 effluent of VFCW was electrochemically treated in duplicate for kinetic studies.

## 2.4. Vertical-flow constructed wetlands (VFCW)

Three lab-scale VFCWs were built based on the design of He et al. (2018) and used for treating the raw CTBD, effluent from EO/BDD, and EO/MMO cell treatment. The VFCWs (Fig. 1) were built-in glass aquariums with a volume of 0.015 m<sup>3</sup> (0.25 × 0.25 × 0.25 m) of which the sides were covered with a fabric that was impenetrable by light to prevent algae growth. The VFCWs were composed of three layers. The top and bottom layers consisted of 4 cm of 8–16 mm gravel (GAMMA, Wageningen, the Netherlands) that allowed proper distribution of the influent and drainage of the effluent. The middle part consisted of a 16 cm thick layer of sand with an average diameter of 0.2 mm (GAMMA, Wageningen, the Netherlands). The VFCWs were planted with *Phragmites australis* since this plant species grow well in CWs fed with CTBD (Wagner et al., 2020a). The VFCWs were kept in a climate chamber (Heraeus Vötsch MC 785-KLIMA) operated at 18 (±1) °C, relative humidity of 75 (±5)% and 10 h of daily light exposure by fluorescent lamps (58 W, 400–800 nm, 645 lx).

Before the addition of CTBD, the VFCWs were fed with synthetic municipal wastewater composed of urea (30 mg/L), K<sub>2</sub>PO<sub>4</sub> (28 mg/L), NaCl (7 mg/L), CaCl<sub>2</sub>·2H<sub>2</sub>O (4 mg/L) and MgSO<sub>4</sub>·7H<sub>2</sub>O (2 mg/L) for two months to enable the development of a microbial community capable of degrading OCs. Subsequently, all VFCWs were fed with raw CTBD for 15 days to acclimatise to CTBD, after which the performance assessment and date counting started. For scenario 1 (VFCW-EO), one of the VFCWs was fed with untreated CTBD for 90 days. For scenario 2 (EO-VFCW), the EO/BDD-VFCW and EO/MMO-VFCW systems were fed with the effluent of the EO experiments for 42 days. For the EO-VFCW experiments, CTBD was treated by EO every 3-day to obtain fresh EO-treated CTBD with a consistent composition. All the VFCWs were fed manually and completely emptied every 3 days to obtain a hydraulic retention

**Table 1**

Characteristics of cooling tower blowdown (CTBD) used in this study.

Parameter	Avg.	SD (±)	Unit
Conductivity	3.4	0.1	mS/cm
Cl <sup>-</sup>	458	10	mg/L
NO <sub>3</sub> <sup>-</sup>	57	1.8	mg/L
SO <sub>4</sub> <sup>2-</sup>	1043	52	mg/L
Na <sup>+</sup>	334	2.9	mg/L
Ca <sup>2+</sup>	338	7.6	mg/L
Mg <sup>2+</sup>	58	2.4	mg/L
K <sup>+</sup>	75	1.3	mg/L
TOC	41	1.3	mg/L
COD	107	6.4	mg/L
Benzotriazole	0.8	0.1	mg/L
AOX	3.2	0.2	mg Cl <sup>-</sup> /L
Bioluminescence inhibition	<5%		(%)
pH	6.8	0.2	

time of 3 days. This 3-days hydraulic retention time was based on earlier experience of our research group with CWs treating CTBD (Wagner et al., 2020c). The VFCW effluent volume was compared with the influent volume to determine the evapotranspiration of the CWs during the entire experiment period (Table S1). Samples for COD and TOC measurements were taken every three days.

## 2.5. Cooling tower blowdown (CTBD) composition

Real CTBD was obtained from a cooling tower of Dow Benelux BV (Terneuzen, The Netherlands). During the operation of the cooling tower, cooling tower water is prepared from local surface water by sand filtration. Sulfuric acid is added to the treated surface water to adjust the pH. Benzotriazole is added to the treated surface water to prevent corrosion. Additionally, phosphonate antiscalants are added to prevent scaling, and biocides are added to inhibit microbiological activity (Koeman-Stein et al., 2016). After a salt concentration threshold is reached, the treated surface water is discharged as CTBD. The CTBD used in the present study was obtained during a regular discharge episode. The obtained CTBD was stored at 4 °C to prevent the growth of microorganisms and was subsequently used in all experiments without any pre-treatment. The characteristics of the CTBD are provided in Table 1.

## 2.6. Analytical methods

### 2.6.1. COD and TOC

Chemical oxygen demand (COD) and total organic carbon (TOC) of every effluent batch were measured for both scenarios. COD was measured by Hach Lange kit LCK-314 (Hach Lange GmbH, Düsseldorf, Germany), and TOC was analysed by a TOC-L<sub>CPH</sub> analyser connected to an ASI-L autosampler (Shimadzu, 's Hertogenbosch, The Netherlands). A 680° catalytic oxidation – non-dispersive infrared detection method was used.

### 2.6.2. Ions determination

Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were measured by ion chromatography (IC) on an ICS 2100 (Dionex, Breda, The Netherlands) equipped with a Dionex IonPac AS19 column (4 × 250 mm) using a hydroxide gradient. ICP-OES AVIO 500 (Perkin Elmer, USA) was used for Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> analysis.

### 2.6.3. Benzotriazole

Benzotriazole was measured by LC-MS/MS. The sample injection volume was 20 µL. Chromatographic separation was achieved with a Shim-pack XR-ODSIII C18-column (50 × 2 mm with a particle size of 1.6 µm) (Shimadzu, 's-Hertogenbosch, the Netherlands) installed in a Prominence LC consisting of two LC-20CE XR pumps, a SIL-20AC XR auto-sampler, and a CTO-20AC column oven. The

mobile phase consisted of solvent A: H<sub>2</sub>O with 0.1 % acetic acid and solvent B: methanol. A 4.5 min gradient elution method was used with an increase from 10 % B to 100 % B in 2.5 min, 100 % B for 1.5 min, and a decrease from 100 % B to 10 % B in 0.5 min. The flow rate was 0.3 mL/min, and the column temperature 35 °C. The system was allowed to equilibrate for 2.5 min prior to each sample injection. Mass spectrometry was performed on a 4000 QTRAP MS/MS system (AB Sciex, MA, USA) coupled to an ESI interface operating in positive mode. Data acquisition and analysis were performed with AB Sciex Analyst software (version 1.5.1, AB Sciex, USA). Benzotriazole was identified and quantified by multiple reaction monitoring (MRM) using fragment ions 120/65 and 120/92 and an 11-point external calibration line (0.1–20 µg/L). The lowest point of the calibration line (0.1 µg/L) corresponded with the limit of quantification for benzotriazole.

#### 2.6.4. Adsorbable organic halides (AOX)

The formation of AOX was determined with the LCK 390 AOX Cuvette Test (Lange GmbH, Düsseldorf, Germany) according to the test protocol provided by the manufacturer. In short, AOX compounds were adsorbed on a carbon disk, after which it was rinsed with solvent to remove the inorganic carbon before digestion for two hours at 100 °C. Finally, the AOX concentration was measured by a DR 3900 spectrophotometer (Lange GmbH, Düsseldorf, Germany).

#### 2.6.5. Microtox toxicity tests

The bioluminescence inhibition of marine bacteria *Vibrio fischeri* was by Microtox<sup>®</sup> test kits (Microlan, the Netherlands) and an M200 Infinite Pro Microplate Reader (Tecan, Switzerland). The bacteria were exposed to the effluent samples of the different scenarios for 15 min at room temperature and in darkness. CuSO<sub>4</sub> as Cu (II) and raw CTBD were used as a negative control and blank control, respectively.

### 2.7. Data analysis

#### 2.7.1. Removal efficiencies

A distinction was made between the mass-based removal efficiency (*mbRE*) and concentration-based removal efficiency (*cbRE*) for the different treatment systems. The *cbRE* for COD and TOC was calculated according to Eq. (1):

$$cbRE = \left( \frac{C_{inf} - C_{eff}}{C_{inf}} \right) \times 100\% \quad (1)$$

In Eq. (1),  $C_{inf}$  and  $C_{eff}$  are the influent and effluent concentration in mg/L.

The *mbRE* for COD and TOC were calculated according to Eq. (2):

$$mbRE = \left( \frac{m_{inf} - m_{eff}}{m_{inf}} \right) \times 100\% \quad (2)$$

In Eq. (2),  $m_{inf}$  is the influent mass in mg, derived from the volume and concentration of the influent, and  $m_{eff}$  is the effluent mass derived from the volume and concentration of the effluent.

The combined mass-based removal efficiency (*mbRE<sub>c</sub>*) of the treatment-combinations is expressed as Eq. (3) (supporting calculations are provided in the SI text 1):

$$mbRE_c = mbRE_1 + mbRE_2 - (mbRE_1 \times mbRE_2) \quad (3)$$

In Eq. (3), *mbRE<sub>1</sub>* is the 1st step removal efficiency and *mbRE<sub>2</sub>* is the 2nd step removal efficiency.

#### 2.7.2. Energy consumption during electrochemical oxidation

The energy consumption by EO (kWh/kg COD) was calculated according to Eq. (4)

$$\text{Energy consumption} = \frac{\Delta E_{cell} \times I \times t}{1000 \times V_s \times \Delta COD} \quad (4)$$

Where:  $V_s$  is electrolyte volume (m<sup>3</sup>),  $I$  is the applied current (A),  $t$  is the electrolysis time (h),  $\Delta E_{cell}$  is the average cell voltage (V) and  $\Delta COD$  is the cbCOD removal during the oxidation time (kg COD/m<sup>3</sup>)

### 3. Results and discussion

In the following sections, the treatment efficiency of the integrated EO-CW systems will be discussed according to the two scenarios described in section 2.2.

#### 3.1. Constructed wetland treatment followed by electrochemical oxidation

In Scenario 1, raw CTBD was fed to the VFCWs, after which it was treated by EO with a BDD- or an MMO-anode. The performance of this scenario is provided in Table 2.

##### 3.1.1. COD and TOC removal in the vertical-flow constructed wetland

During the first two weeks of operation, the cbRE for COD was around 60 % (Fig. 2a). However, the cbRE decreased in the subsequent 45 days. The COD concentration in the VFCW effluent was higher than the VFCW influent concentration after 51 days of operation, probably due to a substantial amount of evapotranspiration by *Phragmites australis* in the VFCW resulting in a concentrated VFCW effluent. On average, 32 (±3)% of the influent water evaporated from the VFCW under controlled climate conditions (Table S1). A similar declining trend of the COD cbRE caused by evapotranspiration in a VFCW was reported by Grafias et al. (2010) for the treatment of olive pomace leachate by VFCW-EO. In that study, the COD cdRE also dropped substantially after initial removal, and effluent COD concentrations became similar to the influent COD concentration within 60 days of operation. A substantial amount of evapotranspiration of CTBD in the VFCW would result in a lower CTBD reuse efficiency and should, therefore, be avoided.

The *mbRE* of COD was calculated (Fig. 2b) to correct the COD concentrations for the evaporation. The *mbRE* decreased from ~65 % during the first week of operation to ~10 % after 45 days of operation (Fig. 2b). After 60 days, the CTBD loading was varied to observe the response in the removal efficiency of the VFCW. The effluent COD concentration continued to increase, while the *mbRE* of COD fluctuated with the loading, indicating that part of the COD was removed, but that evapotranspiration caused a higher effluent concentration than influent concentration.

The TOC removal showed similar trends in *cbRE* and *mbRE* as the removal of COD (Fig. 2c; 2d). During the first days of operation, the TOC *cbRE* was ~50 %. However, the TOC *cbRE* decreased day by day, and the effluent TOC concentration became higher than the influent TOC concentration after 60 days (Fig. 2c). The *mbRE* of TOC decreased from ~60 % during the first 15 days to ~0 % after 60 days (Fig. 2d).

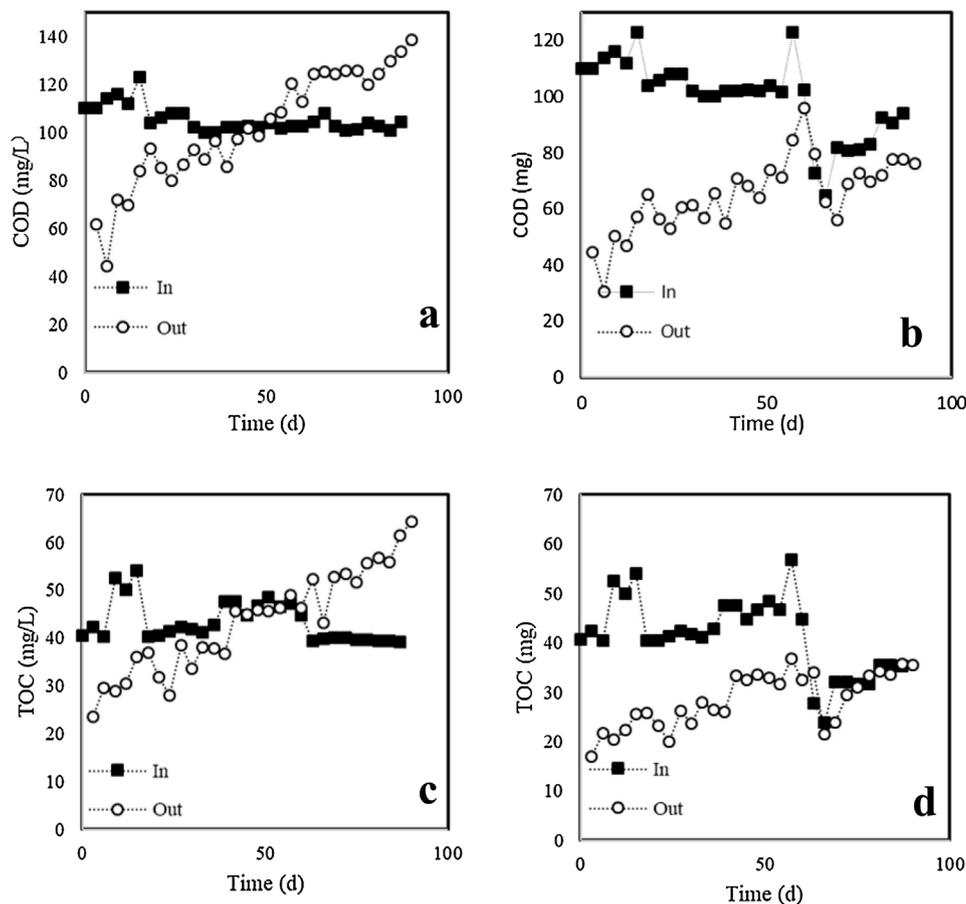
The removal of TOC / COD in CWs is the result of various removal processes and mainly depends on the form of the organic fraction (Garcia et al., 2010). The dissolved organic fraction can be removed by biodegradation, adsorption, and plant uptake, while the particulate organic matter fraction is retained in a CW by physical filtration. The TOC of the CTBD in the present study mainly consists of humic acids (Löwenberg et al., 2015). It was observed by Wagner et al. (2020c) that the particulate humic acid fraction of synthetic CTBD was retained by physical filtration. However, the humic acids in

**Table 2**  
Performance of treatment scenario 1: Vertical-flow constructed wetland (VFCW) followed by electrochemical oxidation (EO) with boron-doped diamond (BDD) or mixed-metal oxide (MMO) anodes. mbRE = mass-based removal efficiency.

Performance evaluation parameter	CW followed by EO/BDD			CW followed by EO/MMO		
	CW Step ( $\pm$ SD)	EO step ( $\pm$ SD)	Combine CW-EO/BDD	CW step ( $\pm$ SD)	EO step ( $\pm$ SD)	Combine CW-EO/MMO
COD mbRE (%)	47 (11) <sup>a</sup>	95 (5) <sup>b</sup>	97	47 (11) <sup>a</sup>	55 (5) <sup>b</sup>	76
TOC mbRE (%)	46 (9) <sup>a</sup>	28 (6) <sup>b</sup>	61	46 (9) <sup>a</sup>	8 (1) <sup>b</sup>	50
<sup>b</sup> Benzotriazole (%)	97 (0.1)	100	100	97 (0.1)	100	100
<sup>b</sup> Bioluminescence inhibition (%)	10 (3)	>95	–	10 (3)	>95	–
<sup>b</sup> AOX (mg Cl <sup>-</sup> /L)	2.4 (1)	18 (2)	–	2.4 (1)	19 (2)	–
<sup>b</sup> ClO <sub>3</sub> <sup>-</sup> (mg/L)	0	197 (14)	–	0	79 (3)	–
<sup>b</sup> ClO <sub>4</sub> <sup>-</sup> (mg/L)	0	39 (3)	–	0	0	–

<sup>a</sup> Average of 15 measurements (3–45 days).

<sup>b</sup> Average of 3 measurements (3–15 days).



**Fig. 2.** Vertical-flow constructed wetlands (VFCW) performance during original CTBD treatment. (a) concentration-based COD; (b) mass-based COD; (c) concentration-based TOC; (d) mass-based TOC.

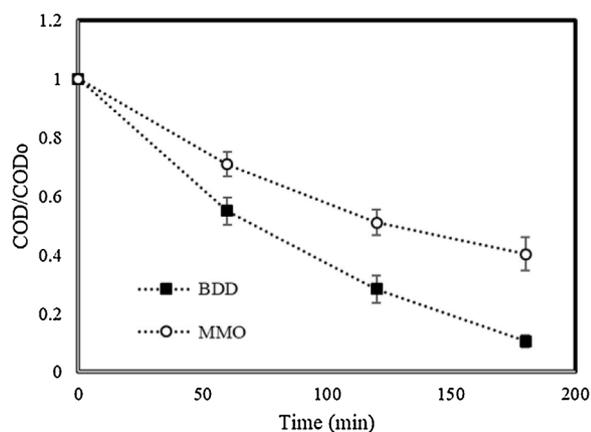
the real CTBD in the present study were better dissolved and thus needed to be removed by biological and chemical rather than physical removal mechanisms, such as biodegradation and adsorption to the CW substrate. However, humic acid is recalcitrant to biodegradation (Almendros and Dorado, 2001), and this would explain the low mbRE of COD / TOC consisting of humic acids in the VFCW system.

The benzotriazole cbRE of the VFCW was 97 ( $\pm$ 0.1)% (Table 2), despite the substantial impact of the evapotranspiration on the COD and TOC removal efficiencies. This benzotriazole removal from CTBD in subsurface CWs is the result of simultaneously occurring adsorption and biodegradation (Wagner et al., 2020c). The complexation of benzotriazole and Ca<sup>2+</sup> ions that are present in the CTBD (Table 1) increases the adsorption of benzotriazole to the sediment (Bi et al., 2007; Wagner et al., 2020c). VFCWs have a

higher benzotriazole removal efficiency than horizontal flow CWs (Matamoros et al., 2010; Kahl et al., 2017; Nivala et al., 2019; Wagner et al., 2020b), as result of the prevailing aerobic conditions in the VFCW allowing aerobic biodegradation to occur.

### 3.1.2. COD removal by electrochemical oxidation post-treatment

VFCW pre-treated CTBD was treated by EO with a BDD or MMO anode, and the COD cbRE with the BDD-anode was 95 ( $\pm$ 5)% after 3 h of oxidation (Fig. 3). With the MMO-anode, the COD cbRE was only 55 ( $\pm$ 5)% after the same time of operation (Fig. 3). The COD removal occurred with the first-order reaction kinetics with a linear regression coefficient of >0.99 for both anodes (Fig. S1). The rate constants were  $1.3 \times 10^{-2}$  /min for the BDD-anode and  $4.8 \times 10^{-3}$  /min for the MMO-anode.



**Fig. 3.** COD removal during the electrochemical oxidation (EO) of Day-3 VFCW effluent. COD: 61 mg/L, Conductivity: 4.8 mS/cm, pH: 7.08, Applied current density: 5.5 mA/cm<sup>2</sup> for BDD anode and 8.7 mA/cm<sup>2</sup> for MMO anode.

**Table 3**

Possible radicals and active chlorinated species formed during electrochemical oxidation.

Equation No	Reaction	Reference
1	$H_2O \rightarrow \bullet OH + H^+ + e^-$	Lan et al. (2017)
2	$SO_4^{2-} + \bullet OH \rightarrow SO_4^{\bullet -} + OH^-$	
3	$Cl^- + \bullet OH \rightarrow Cl^{\bullet} + OH^-$	
4	$2Cl^{\bullet} \rightarrow Cl_2$	
5	$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$	
6	$HOCl \leftrightarrow ClO^- + H^+$	

The calculated rate constants show that the BDD-anode performed better than the MMO-anode. The water oxidation potential of the BDD-anode is 2.3 V vs. SHE (standard hydrogen electrode), whereas it is 1.47 V vs. SHE for a MMO-anode (Panizza and Cerisola, 2009). Therefore, the active hydroxyl, sulfate, and chlorine radicals' formation according to equations 1–3 (Table 3) is more efficient with the BDD-anode. These radicals can quickly oxidise the OCs in the CTBD, which reduces the COD concentration (Lan et al., 2017).

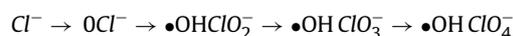
In contrast, the radical formation with the MMO-anode is limited due to the low water oxidation potential. However, it was reported by different authors (de Moura et al., 2014d; Fajardo et al., 2017) that active chlorinated species, such as hypochlorite, can be formed in the bulk liquid with the MMO-anode according to reaction equations 4–6 (Table 3). These active chlorinated species can oxidise the OCs in the CTBD. However, the oxidation potential of these active chlorinated species is lower than the oxidation potential of the radicals. Therefore, the COD removal was slower with the MMO-anode than with the BDD-anode, which was also reflected in the energy consumption (table S2) during the EO. The energy consumption was 19 kW h/kg COD for the EO/BDD system, whereas it was 64 kW h/kg COD for the EO/MMO system.

### 3.1.3. The overall treatment performance of scenario 1

The COD mbRE of the integrated VFCW-EO/BDD system was 97 %, while the TOC mbRE was 61 % (Table 2). The VFCW-EO/MMO system had a COD mbRE of 55 (±5)% and a TOC mbRE of 50 % (Table 2). EO-treatment after the VFCW by both anodes was capable of removing the remaining benzotriazole (Table 2). Hence, VFCW-EO/BDD treatment removed a substantial amount of OCs from the CTBD that could hinder physico-chemical CTBD desalination, despite the large loss in water volume as a result of evapotranspiration in the VFCW.

The toxicity of the CTBD in terms of bioluminescence inhibition of *Vibrio fischeri* showed an increase after VFCW-EO treatment. The untreated CTBD had a bioluminescence inhibition of ~5%. After

VFCW-treatment, the bioluminescence inhibition increased to 10 (±3)% (Table 2) demonstrating a slight increase in toxicity of the VFCW-treated CTBD to *Vibrio fischeri*. This might have been a result of evapotranspiration and a corresponding increase of the electrical conductivity from 3.4 mS/cm to ~4.8 mS/cm. In contrast, the bioluminescence inhibition increased to 95 % (Table 2) after the EO-treatment with both anodes, which indicated high toxicity of the treated CTBD to *Vibrio fischeri* as a result of EO. This increased toxicity was the result of the formation of chlorinated organic compounds (AOX) and chlorinated inorganic compounds that are toxic to *Vibrio fischeri* (Bergmann et al., 2014). The AOX concentration increased from 2.4 (±1) to 18–19 mg Cl<sup>-</sup>/L after EO-treatment by both anodes (Table 2). Also, 197 (±14) mg/L of ClO<sub>3</sub><sup>-</sup> and 39 (±3) mg/L ClO<sub>4</sub><sup>-</sup> were formed with the BDD-anode. With the MMO-anode, only 79 (±3) mg/L of ClO<sub>3</sub><sup>-</sup> was produced (Table 2). De Moura et al. (2014) showed that EO of chloride-containing water with RuO<sub>2</sub>-MMO-anodes could produce hypochlorite (ClO<sup>-</sup>) and ClO<sub>3</sub><sup>-</sup> from chloride. Perchlorate (ClO<sub>4</sub><sup>-</sup>) was found during the EO of chlorinated wastewater with a BDD-anode according to the following steps (Lan et al., 2017)



Similarly, Garcia-Segura et al. (2015) observed that high concentrations of ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and lower concentrations of AOX were formed during EO-treatment of secondary effluent with a BDD-anode. AOX, ClO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> are responsible for increasing the toxicity of the treated CTBD (Bergmann et al., 2014). In conclusion, VFCW-EO treatment does result in a substantial OCs removal but produces undesired chlorinated products that increase the CTBD toxicity. Therefore, these undesirable chlorinated products need to be removed during subsequent physico-chemical desalination steps before reuse.

### 3.2. Scenario 2: Electrochemical oxidation followed by vertical-flow constructed wetlands

In Scenario 2, raw CTBD was electrochemically treated with the BDD-anode or the MMO-anode for 3 h after which EO effluent was fed to the VFCWs. The performance of this scenario is provided in Table 4.

#### 3.2.1. COD removal during electrochemical oxidation of original CTBD

EO-treatment with the BDD-anode resulted in a COD mbRE of 81 (±5)%, while the COD mbRE with the MMO-anode was 47 (±6)% (Fig. 4). Similar to scenario 1 (section 3.1), the BDD-anode has a higher COD mbRE than the MMO-anode due to the efficient formation of radicals with the BDD-anode.

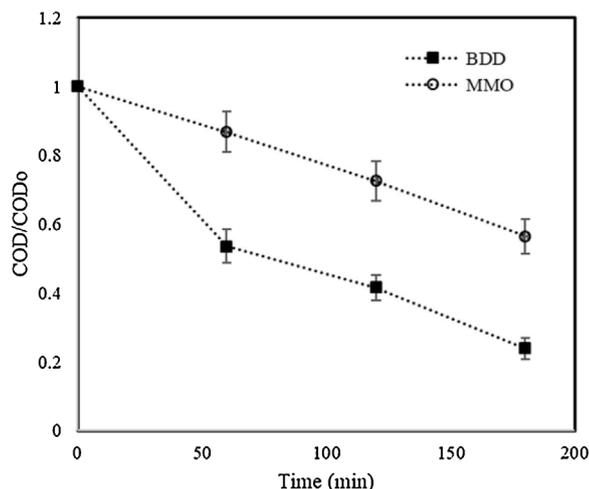
The COD removal with the BDD-anode was a two-phase process in which COD was quickly removed during the first hour, after which the removal rate decreased (Fig. 4). This two-phase phenomenon, which was also seen in our earlier study (Saha et al., 2020), can be explained by the radical formation process at the anode surface and the diffusion of the OCs towards the anode surface. Several researchers stated that radicals are formed very close to the BDD-anode surface (Martínez-Huitle and Panizza, 2018). Therefore, the reaction between the radicals and the OCs occurs only on the surface of the BDD-anode (Song et al., 2018). As a result, the oxidation of OCs is mass transfer limited and depends on the OCs concentration. It can be assumed that the radical formation controlled the first-hour reaction rate in the present study and that the OCs transport was fast enough to prevent mass transfer limitation in the system. As the reaction proceeds, OCs are oxidised, and the OCs concentration decreases, after which mass transfer limitation slows down the OCs oxidation rate. A similar phenomenon

**Table 4**  
Performance of treatment scenario 2: Electrochemical oxidation (EO) with boron-doped diamond (BDD) and mixed-metal oxide (MMO) anodes followed by vertical-flow constructed wetland (VFCW). mbRE = mass-based removal efficiency.

Performance evaluation parameter	EO_BDD followed by CW			EO_MMO followed by CW		
	EO step ( $\pm$ SD)	CW Step ( $\pm$ SD)	Combine EO/BDD-CW	EO step ( $\pm$ SD)	CW step ( $\pm$ SD)	Combine EO/MMO-CW
<sup>a</sup> COD mbRE (%)	81 (5)	−25 (31)	76	47 (6)	18 (32)	57
<sup>a</sup> TOC mbRE (%)	41 (5)	12 (23)	48	11 (4)	18 (29)	27
<sup>b</sup> Benzotriazole (%)	100	–	100	75 (10)	100	100
<sup>b</sup> Bioluminescence inhibition (%)	>95	27(17)	–	>95	14 (16)	–
<sup>b</sup> AOX (mg Cl <sup>−</sup> /L)	15 (2)	3 (1)	–	24 (2)	5 (2)	–
<sup>b</sup> ClO <sub>2</sub> <sup>−</sup> (mg/L)	183 (4)	118 (7)	–	99 (11)	29 (6)	–
<sup>b</sup> ClO <sub>4</sub> <sup>−</sup> (mg/L)	35 (1)	24 (1)	–	0	0	–

<sup>a</sup> Average of 14 measurements (3–42 days).

<sup>b</sup> Average of 3 measurements (3–15 days).



**Fig. 4.** COD concentration over time during electrochemical oxidation (EO) of original CTBD. Average COD: 107 mg/L, Conductivity: 3.4 mS/cm, pH: 6.8, Applied current density: 5.5 mA/cm<sup>2</sup> for BDD anode and 8.7 mA/cm<sup>2</sup> for MMO anode.

was observed during COD removal from phenolic wastewater with a BDD-anode (Oliveira et al., 2018). Another reason for the two-phase OCs removal process might be that the OCs are oxidised into different intermediates during the oxidation, such as organic acids and chlorinated organics (Punturat and Huang, 2017). These intermediates are less favourable for oxidation, which ultimately causes a complicated COD removal profile with the BDD-anode (Mao et al., 2012; Yao et al., 2019).

For the MMO-anode, the COD mbRE from untreated CTBD was similar to the COD mbRE from VFCW pre-treated CTBD. The COD removal by the MMO-anode was facilitated by active chlorinated species, such as hypochlorite (ClO<sup>−</sup>). In our previous study, 205 ( $\pm$ 5) mg/L of hypochlorite expressed as Cl<sub>2</sub> was formed during direct EO of CTBD with an MMO-anode at 8.7 mA/cm<sup>2</sup> current density, which was three times higher than the formation of ClO<sup>−</sup> with a BDD-anode at 5.5 mA/cm<sup>2</sup> current density (Saha et al., 2020). Thus, with the MMO-anode, the OC removal was dominated by active chlorine species, which have two times less oxidation potential as compared to the hydroxyl radical that is produced by the BDD-anode.

The benzotriazole mbRE of the BDD-anode was 100 %, while the MMO-anode had a benzotriazole mbRE of 75 ( $\pm$ 10)%. Wu et al. (2015) showed that benzotriazole degradation by a BDD-anode was faster than by a PbO<sub>2</sub> (MMO)-anode because the BDD-anode has higher catalytic activity, and the hydroxyl radical has a lower affinity to be adsorbed to the electrode surface as compared to the PbO<sub>2</sub>-anode. The same authors also showed that not only hydroxyl radicals, but also other active species were responsible for benzotriazole removal in the EO-system. Hence, a substantial amount of

benzotriazole was removed by the active chlorine species produced with the MMO-anode.

The energy consumption by EO before VFCW-treatment was higher than the energy consumption by EO after VFCW-treatment (Table S2). The energy consumption was 19 % higher in the EO stage of EO-VFCW compared with the VFCW-EO system for both anodes. Lower energy consumption of EO-system treating VFCW-treated CTBD was attributed to the increased CTBD electrical conductivity after VFCW-treatment as a result of evapotranspiration, which decreased the internal resistance in the EO cell (Tian et al., 2011).

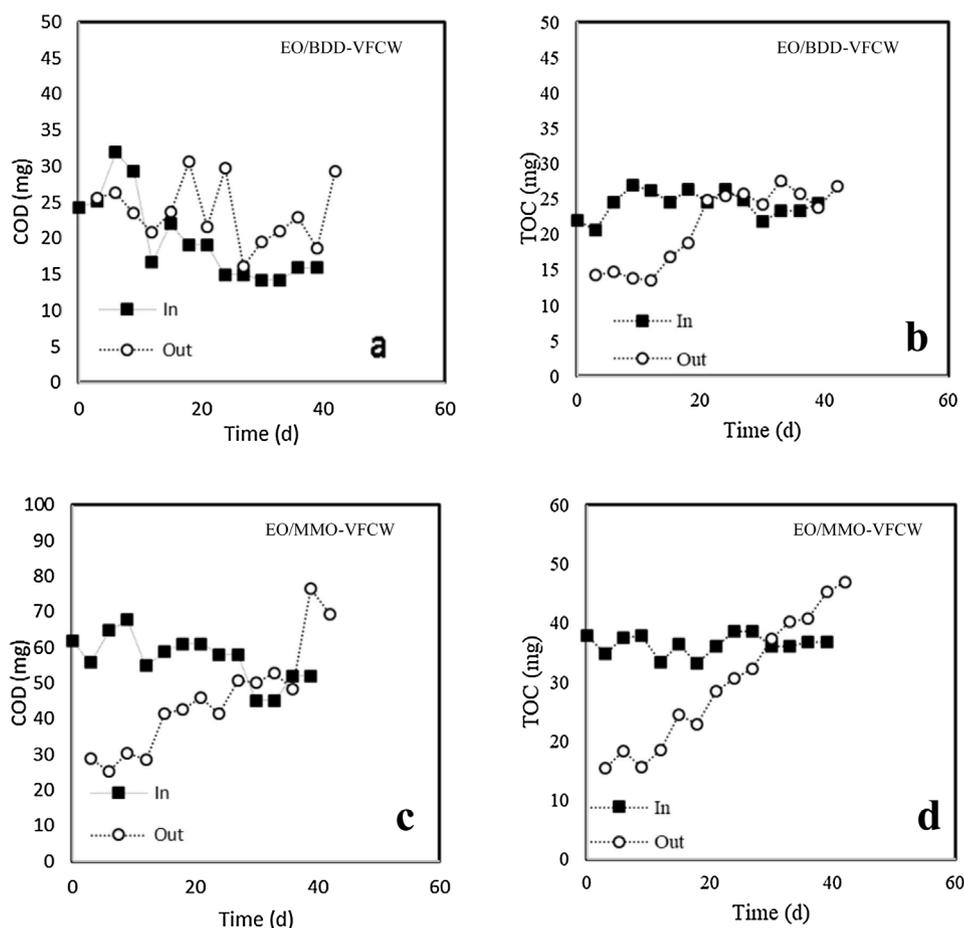
### 3.2.2. Treatment of electrochemically oxidised CTBD by the VFCW

The COD mbRE did not increase after VFCW-treatment of EO-treated CTBD (Fig. 5a) for the BDD-anode. The COD concentration in the VFCW effluent was higher than in the influent except for the first 15 days. The COD mbRE from the BDD-treated CTBD in the VFCW ranged from −85 % to 29 % (Fig. 5a). The TOC mbRE in the VFCW ranged from −30 % to 50 % (Fig. 5b). This illustrates that VFCW treatment does not contribute substantially to OCs removal after EO/BDD. The COD mbRE in the VFCW treating MMO-treated CTBD decreased from 55 % to −48 % during the 42-day experimental period, while the TOC mbRE decreased from 60 % to −28 % (Fig. 5c; d). Apparently, EO by both anodes does not result in an OCs fraction that is more readily biodegradable for microorganisms in the VFCW than the initial OCs fraction of the CTBD.

### 3.2.3. The overall treatment performance of scenario 2

The average overall COD mbRE in the EO/BDD-VFCW was 76 %, while the average TOC mbRE was 48 % during 42 days of operation (Table 4). In the EO/MMO-VFCW, the average overall COD mbRE was 57 %, while the average TOC mbRE was only 27 % (Table 4). During direct CTBD treatment by the VFCW in scenario 1, the mbRE of COD and TOC were not negative during the entire experiment period (Table 2). In contrast, the VFCW mbRE for COD and TOC became negative after 20–30 days of operation in scenario 2. The lower VFCW mbRE can be attributed to the formation of chlorinated organic and inorganic by-products during EO treatment that hampers normal VFCW functioning. Chlorinated compounds are toxic and may inhibit the microbial activity in the CW (Bhatt et al., 2007), resulting in a lower biodegradation efficiency. Besides, EO by-products could be less susceptible to biodegradation in VFCWs than the original OCs in the CTBD. However, this would not explain a negative COD mbRE. The negative mbRE might be attributed to the decay and leaching of plant root material and microbial biofilms that died due to the toxicity of EO pre-treated CTBD, thus increasing the COD concentration in the effluent.

An additional hint for an increase in the toxicity of the EO treated CTBD is the bioluminescence inhibition of *Vibrio fischeri*, which increased drastically from 5% to >95 % for both anodes after EO.



**Fig. 5.** Vertical-flow constructed wetland (VFCW) performance during electrochemically pre-treated CTBD treatment. (a) mass-based COD and (b) mass-based TOC for EO/BDD-VFCW system; (c) mass-based COD and (d) mass-based TOC for EO/MMO-VFCW system.

As described in section 3.1.3, the bioluminescence inhibition was triggered by the production of AOX,  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  during the EO treatment. Direct EO treatment of CTBD with the BDD-anode indeed produced  $15 (\pm 2)$  mg  $\text{Cl}^-/\text{L}$  AOX,  $182 (\pm 4)$  mg/L  $\text{ClO}_3^-$  and  $35 (\pm 1)$  mg/L  $\text{ClO}_4^-$ . The MMO-anode produced  $24 (\pm 2)$  mg  $\text{Cl}^-/\text{L}$  AOX and  $99 (\pm 11)$  mg/L of  $\text{ClO}_3^-$ . The formation of chlorinated compounds during direct EO of CTBD and EO of VFCW effluent was comparable. Due to the co-existence of all chlorinated species, it was not possible to determine the origin of toxicity.

The VFCW-treatment after EO significantly decreased the bioluminescence inhibition % to  $27 (\pm 17)\%$  for the EO/BDD-VFCW system and  $14 (\pm 16)\%$  for the EO/MMO-VFCW system. The AOX,  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  concentration decreased substantially after VFCW treatment (Table 4). This was because of the reaction of the AOX and chlorinated inorganic species with the substrate of the CW and because of the detoxification capacity of naturally existing microorganisms in CWs through biodegradation reactions (Nozawa-inoue et al., 2005; Bhatt et al., 2007; Carlström et al., 2015). However, the *Phragmites australis* in the VFCWs was not able to cope with the EO treated CTBD. Plants grown in untreated CTBD did not show visual abnormalities during the experimental period. However, the plants fed with EO/MMO and EO/BDD treated CTBD showed signs of discoloration and eventually died. The plant's death was likely the result of the toxicity of the electrogenerated chlorinated intermediate compounds. The plants in the VFCW were in the first stage of their development. More studies are needed to determine whether electrogenerated chlorinated species have a similar impact on more mature VFCW systems with better-developed plants. In addition, unplanted VFCW systems might be used as a first treatment step in

a multi-component CW to deactivate the toxic chlorinated intermediates.

#### 4. Conclusions

The reuse of cooling tower blowdown (CTBD) in the cooling tower itself requires physico-chemical desalination preceded by a proper pre-treatment that removes organic chemicals (OCs). In this research, the removal of OCs from CTBD using combined systems of electrochemical oxidation (EO) with boron-doped diamond (BDD)- and mixed-metal oxide (MMO)-anodes and vertical-flow constructed wetlands (VFCWs) were evaluated. The VFCW was effective in removing specific conditioning chemicals, such as benzotriazole, from CTBD. However, the removal of bulk OCs in VFCWs was low, since the OCs in CTBD consisted of recalcitrant humic substances. EO-treatment after VFCW-treatment increased the OCs removal, especially with the BDD-anode. However, EO of the VFCW effluent resulted in the production of toxic chlorinated organic and inorganic species, and therefore the VFCW-EO effluent should be further treated to reduce its toxicity. Direct EO of the CTBD followed by VFCW-treatment resulted in the death of the plants in the CTBD as a result of the production of unwanted toxic by-products, but a decrease in the toxicity of the combined effluent. For future research, it is recommended to identify the exact source of the toxic effect to VFCW plants and to identify ways to mitigate this effect, because EO-VFCW produces a less toxic final product. Besides, EO methods that do not produce toxic chlorinated by-products should be developed to avoid related toxicity problems. Also, evapotranspiration should be minimised for maximal water recovery.

## Declaration of Competing Interest

The authors confirmed no conflict of interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.psep.2020.07.019>.

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