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ABSTRACT

Large volumes of freshwater are used globally for cooling towers. The reuse of discharged cooling tower water in cooling towers itself could mitigate freshwater scarcity problems. Prior to its reuse, the cooling tower blowdown has to be desalinated. However, physicochemical desalination techniques are hampered by conditioning chemicals (CC) that are added to the cooling tower water circuit to prevent corrosion, mineral scaling, and biofouling and can damage physicochemical desalination equipment. The potential of constructed wetlands (CWs) for the cost-effective removal of these CC prior to desalination is discussed in this review. The characteristics of CWs that determine their suitability for the removal of CC from cooling tower blowdown are elucidated, such as multiple removal pathways working simultaneously. In addition, specific challenges for the design of a constructed wetland for cooling tower blowdown treatment are reviewed, such as configuration options, the toxicity of CC, and the formation and removal of harmful byproducts.

GRAPHICAL ABSTRACT
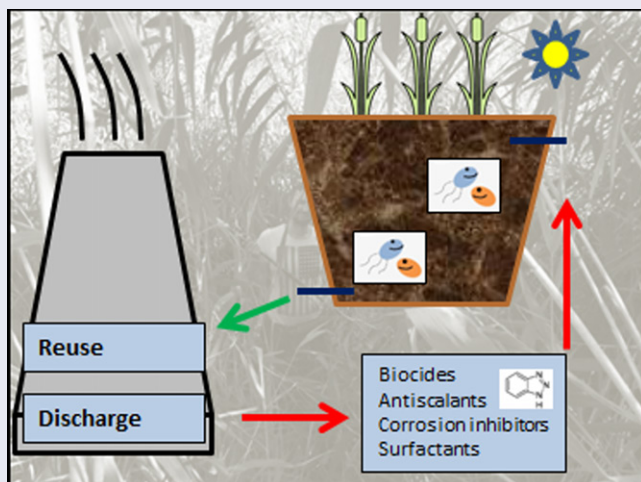
1. Introduction

Lowering the industrial fresh water footprint will contribute to the mitigation of future fresh water scarcity problems. Large volumes of water are utilized by the industrial sector and subsequently discharged back into water bodies after use, with or without treatment (Flörke et al., 2013; Oki & Kanae, 2006). The reuse of these water streams for agricultural or industrial purposes could have a positive impact on ecosystem sustainability, social and economic development, and human health by effectively reducing the quantities of fresh water extracted from aquifers and surface waters (Corcoran et al., 2010).

The reuse of cooling water is an attractive option to lower the freshwater consumption of large industrial operations. The use of cooling water systems for temperature control is common in many industries and in electricity generation (Feeley et al., 2008; Ponce-Ortega, Serna-González, & Jiménez-Gutiérrez, 2010). High volumes of fresh water are consumed for cooling processes. It is estimated that 40–60% of the freshwater consumption by petrochemical industries is used for cooling (dos Santos et al., 2015). After use, this cooling water is generally discharged as cooling tower blowdown (CTBD) to the surface water. Reuse of CTBD in the cooling tower itself could significantly lower its fresh water withdrawal.

Over the past decades, several researchers have studied different methods to reduce the cooling process' fresh water footprint (Altman et al., 2012; Matson & Harris, 1979; Rebhun & Engel, 1988; You, Tseng, Guo, & Yang, 1999; Zhang, Zeng, Ye, Chen, & Yan, 2008). Many of these studies focused

on the reuse of CTBD in the cooling tower itself (Frick, Féris, & Tessaro, 2014; Rebhun & Engel, 1988; You et al., 1999; Zhang et al., 2007). Since reuse of CTBD requires electric conductivity (EC) values below 1000 µS/cm (Groot et al., 2015), the majority of these studies focused on desalination of CTBD by physicochemical water treatment technologies (Zhang et al., 2008; Altman et al., 2012; van Limpt & van der Wal, 2015; Löwenberg et al., 2015). Various studies showed that physicochemical CTBD desalination is hampered by conditioning chemicals (CC) that are present in CTBD (Greenlee, Testa, Lawler, Freeman, & Moulin, 2010; Löwenberg et al., 2015; Sweity, Oren, Ronen, & Herzberg, 2013). CC are used to prevent processes that disturb the cooling process efficiency, such as fouling, scaling, and corrosion. However, these CC hampers various physicochemical desalination technologies by for instance membrane fouling or deterioration of electrode or reactor surfaces. Hence, the removal of CC prior to physicochemical desalination technologies could significantly improve the desalination efficiency and lifespan of desalination equipment.

Several methods for pretreatment prior to physicochemical desalination have been reviewed recently. Löwenberg and Wintgens (2017) analyzed the adsorption to powdered activated carbon prior to ultrafiltration. Pramanik, Roddick, and Fan (2017) reviewed the application of slow sand filtration and biological active carbon prior to ultrafiltration and microfiltration. These pretreatment methods are based on removal mechanisms, such as adsorption and biodegradation. Constructed wetlands (CWs) can be used as nature-based CTBD pretreatment for the removal of CC. CWs are man-made controlled wetland systems that employ similar removal mechanisms as the abovementioned techniques for the removal of contaminants from water streams. In addition, CWs also provide ecological value itself. CWs are generally considered a low-maintenance and cost-effective water *post-treatment* step after conventional wastewater treatment because of their ability to remove a myriad of components from various types of waste water streams. However, the application of CWs for the *pretreatment* of CTBD by removing CC prior to physicochemical desalination is a promising option to optimize physicochemical desalination. The use of CWs can also overcome capacity problems as described by Löwenberg and Wintgens (2017) and Pramanik et al. (2017) that are associated with the large and fluctuating volumes of CTBD. In addition, CWs can be used to buffer large volumes of water to overcome variability in water supply. However, CW systems require relatively large land space. CWs have been used recently for the pretreatment of saline industrial wastewater, which indeed optimized the physicochemical desalination (Huang, Ling, Xu, Feng, & Li, 2011). Pretreatment by the CW reduced the level of iron, manganese, COD, turbidity, and SiO_2, which resulted in less membrane fouling and thus a lower operating pressure and membrane

cleaning frequency. The CW treatment did not result in a reduction of EC, hence desalination was still needed.

The focus of this review will be on the ability of CWs to remove CC from CTBD. Until recently, CWs were approached as "black box" systems. The removal efficiency of a CW was determined by comparing influent and effluent concentrations. The exact removal mechanism for specific contaminants in CWs was not further elucidated. However, several groups recently have worked on identifying specific CW removal mechanisms for mixtures of different contaminants (Ávila, Reyes, Bayona, & García, 2013; He, Sutton, Rijnaarts, & Langenhoff, 2018; He et al., 2017; Jasper & Sedlak 2013; Matamoros, García, & Bayona, 2008; Petrie et al., 2018; Zhang, Gersberg, Ng, & Tan, 2014), which allows a better prediction of the fate of CC from CTBD in the CW. In addition to the removal mechanisms, important parameters that influence CW functioning will be discussed, and challenges for the implementation of CWs for the removal of CC from CTBD will be identified.

2. Conditioning chemicals in cooling tower water

Temperature control is of crucial importance in many industrial processes. In a cooling tower system, heat from industrial processes is transferred into cooling water and subsequently released from the water to dry cold air. Different cooling water system configurations are used throughout industries, such as closed, once-through and recirculation cooling systems (Bott, 1998). In closed cooling systems, water is circulated through closed piping and cooled by a cold air flow. Some closed cooling designs provide an additional cold water spray to enhance the cooling efficiency (Stabat & Marchio, 2004). In these closed cooling systems, the water is not in contact

Table 1. Recirculating CTBD composition.

Parameter ↓	Unit ↓	Davood Abadi Farahani, Borghei, & Vatanpour, et al. (2016)	Groot et al. (2015)*	Löwenberg et al. (2015)*	Zhang et al. (2007; 2008)	Wang, Fan, Xie, and Wang (2006)	Kim, Cho, and Bai (2001)
Temperature	°C		20–30	19.1 ± 1.2	5.0–21.0	4 - 40	
pH	–	6.7–7.2	7.5–8.5	7.9 ± 0.2	8.2–8.75	7.8–9.3	8.2
COD	mg/L	181			3–4.8	0–10	
TOC	mg/L		40–60	59.1 ± 1.5			
EC	μS/cm	2928	3500–4500	3620 ± 810	1300–2000	1650–2100	2150
Turbidity	NTU	73.6		7.3 ± 1.0	5.0–23.0		
TSS	mg/L		<15	12 ± 4.6	7.0–22.0	5–80	
Alkalinity	mg/L CaCO$_3$	1350			350–370		188
Silica	mg/L SiO$_2$			0.9 ± 0.2	50–200		
Chloride	mg/L		400–600	500			404
Phosphate	mg/L		5–15	5.9 ± 1.0	1.1		

*Groot et al. (2015) and Löwenberg et al. (2015) describe the same CTBD. However, some parameters are only provided in one of the two articles.

Table 2. Commonly used CC in cooling tower water.

Biocides	Corrosion inhibitor	Antiscalants
Oxidizing biocides	**Anodic corrosion inhibitor**	Polycarboxylates
Sodium hypochlorite	Chromate	Polyphosphates
Chlorine dioxide	Molybdate	Polyphosphonates
Chloramine	Nitrite	Copolymers
N-bromosuccinimide (NBS)	Orthophosphate	Terpolymers
1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)		
2,4-dibromo-5,5-dimethyldantoin (DBDMH)	**Cathodic corrosion inhibitor**	**Dispersants & surfactants**
Ozone	Polyphosphates	Phosphonates
Peracetic acid	Zinc	Sulfonates
Hydrogen peroxide	Phosphonates	Polyethylene amines
	Calcium carbonates	Monoethanolamine phosphate salts
Non-oxidizing biocides	Silicates	Polycarboxylates
Glutaraldehyde		Copolymers
2,2-dibromo-3-nitrilopropionamide (DBNPA)	**General corrosion inhibitor**	Terpolymers
2-bromo-2-nitro-1,3-propanediol (Bronopol)	(Benzotri)azoles	
Methylisothiazolinone	Organic compounds containing N, S, OH	
1,2-benzisothiazolone (BIT)		
5-chloro-N-methylisothiazolone (CMIT)		
Methylene(bis)thio-cyanate (MBT)		
B-bromo-B-nitrostyrene (BNS)		
Quarternary ammonium compounds (QAC)		

with the environment. In "once-through" systems, fresh water is taken, used in the cooling process, and subsequently discharged into a water body. In recirculating systems, water is taken in and brought in contact with cold air. The cooled water is collected afterwards and reused. Evaporation of part of the cooling water results in increased mineral concentrations in the residual cooling water. High mineral concentrations in the water eventually result in scale formation (Altman et al., 2012; Nanda et al., 2008). To prevent this, the concentrated water is discharged as CTBD after a certain mineral concentration threshold is reached.

CTBD characteristics described in the literature are presented in Table 1. In general, CTBD has a neutral to slightly basic pH and a moderate EC of 1500–4000 µS/cm. In addition, CTBD contains refractory organics, suspended solids and low concentrations of phosphate. After discharge of CTBD, new freshwater, from an external source is added to the cooling water flux to compensate for the water loss. The composition of this "make-up" water must comply with maximum (concentration) values for the EC, phosphates, chloride, and total organic carbon (TOC) (Groot et al., 2015; Rebhun & Engel, 1988). One of the major technological challenges in maintaining proper cooling tower functioning is the mitigation of fouling, scaling, and corrosion as result of the chemical and microbial constituents in the make-up water (Li et al., 2011). CC with different modes of action is used to achieve this, such as biocides, corrosion inhibitors, antiscalants, and surfactants. Table 2 presents the most commonly used chemicals belonging to these classes of CC.

The different classes of CC pose various threats to physicochemical desalination technologies. For instance, scale and corrosion inhibitors cause fouling of reverse osmosis membranes as result of adsorption to the membrane (Greenlee et al., 2010; Sweity, Ronen, & Herzberg, 2014). Biocides damage the structure of reverse osmosis membranes (Vrouwenvelder et al., 2010). Membrane fouling by CC, such as surfactants and antiscalants, is also an issue for the charged membranes in electrodialysis (Guo et al., 2014), and the membranes used in membrane distillation (Tijing et al., 2015; Wang et al., 2008). Hence, knowledge on the relevant removal mechanisms for different classes of CC in CWs allows proper pretreatment prior to physicochemical desalination.

3. Removal of CC from CTBD by CWs

3.1. Contaminant removal mechanisms

As discussed above, the removal of CC from CTBD in CWs could optimize the efficiency of physicochemical desalination processes. Numerous studies report the removal of, example bulk organics (Konnerup, Koottatep, & Brix, 2009; Neralla, Weaver, Lesikar, & Persyn, 2000), nutrients, such as N and P (Lin, Jing, Wang, & Lee, 2002; Vymazal 2007; Zheng et al., 2016), heavy metals (Khan, Ahmad, Shah, Rehman, & Khaliq, 2009; Maine, Sune, Hadad, Sánchez, & Bonetto, 2006), petrochemical constituents (Knight, Kadlec, & Ohlendorf, 1999; Toor, Franz, Fedorak, MacKinnon, & Liber, 2013), and emerging contaminants including pharmaceuticals (Hijosa-Valsero et al., 2011; Li, Zhu, Ng, & Tan, 2014; Rühmland, Wick, Ternes, & Barjenbruch, 2015; Zhang et al., 2012), personal care products (Ávila, Nivala et al., 2014; Matamoros & Bayona, 2006; Reyes-Contreras, Matamoros, Ruiz, Soto, & Bayona, 2011), endocrine disruptors (Ávila, Nivala et al., 2014; Ávila, Bayona, Martín, Salas, & García, 2015), and pesticides (Budd, O'Geen, Goh, Bondarenko, & Gan, 2009; Moore et al., 2009) in CWs. Examples of water streams treated by CWs are domestic waste water (Ye & Li, 2009; Zhao et al., 2011), industrial waste water (Chen, Kao, Yeh, Chien, & Chao, 2006; Ji et al., 2002), and surface water streams (Schulz & Peall, 2001; Zhou & Hosomi, 2008).

The dominant contaminant removal processes in CWs are aerobic and anaerobic biodegradation, photodegradation, plant uptake and further transformation by plants, and sorption to the sediment (see Figure 1) (Brix, 1993; Garcia et al., 2010; Imfeld, Braeckevelt, Kuschk, & Richnow, 2009). The suitability of CWs to treat CTBD is determined by the simultaneous functioning of these removal processes. Determining the dominant removal mechanisms for specific contaminants in CWs allows the prediction of the removal efficiency and the formation of possible toxic transformation

products. This is necessary to design a CW adjusted to the contaminants that need to be removed.

3.2. CW water flow

The water flow in a CW determines the contribution of the different removal mechanisms to the total removal efficiency. Two types of CW can
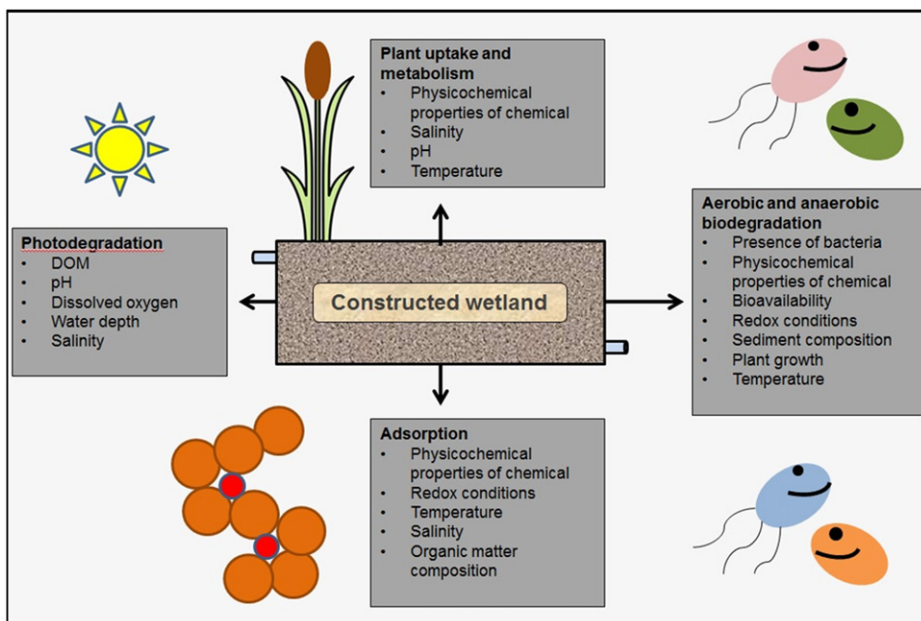

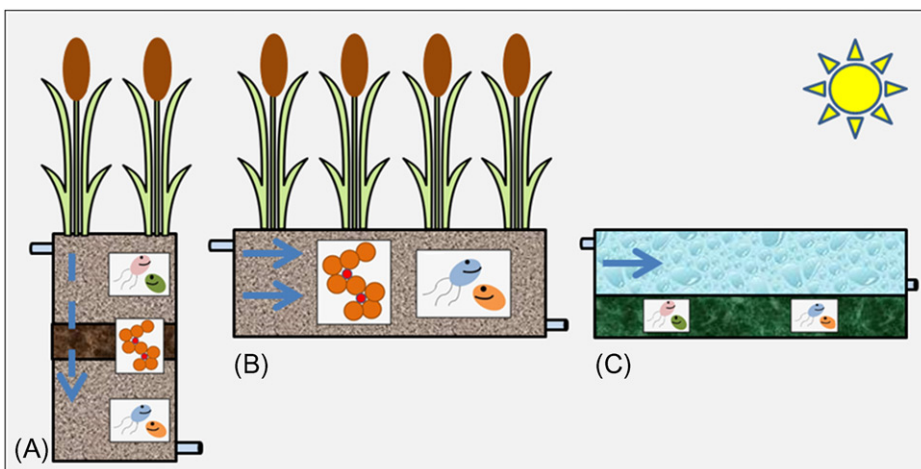**Figure 1.** Main removal mechanisms in CWs and their most influential parameters.

Figure 2. Different water flow types in a CW: (A) a batch-fed vertical flow CW amended with enhanced adsorption substrate layer; (B) a continuously-fed horizontal flow CW; (C) a surface flow CW.

be distinguished based on their water flow: surface water flow or subsurface water flow CWs (Figure 2). In subsurface water flow CWs, water flows below the surface of the CW sediment, where it is in contact with the porous media of the soil, plant roots and rhizomes. Biodegradation, uptake by plants (Vymazal, 2016), and sorption to the sediment matrix are important removal mechanisms in subsurface flow CWs (Dordio & Carvalho, 2013). Both vertical and horizontal subsurface water flow CWs exist. Horizontal subsurface CWs (Figure 2b) are expansive rectangular systems to which the water is continuously fed and then flows horizontally through the subsurface from the inlet to the outlet. Vertical subsurface CWs (Figure 2a) are less space consuming systems to which the water is distributed in batch mode at the top of the CW's sediment and subsequently collected at the bottom. Batch feeding of the vertical flow CWs results in a downward oxygen gradient, to remove contaminants both aerobically and anaerobically. This oxygen gradient can also be established by aeration (Fan, Liang, Zhang, & Zhang, 2013; Wu, Fan et al., 2015).

Surface water flow CWs (Figure 2c) are characterized by a shallow open water surface, with photodegradation and biodegradation as dominating removal mechanisms (Jasper & Sedlak, 2013; Matamoros & Bayona, 2008). Biodegradation in these CWs occurs primarily by biofilms formed on the bottom sediments that can reach a thickness of multiple centimeters (Jasper et al., 2013, Jasper, Jones, Sharp, & Sedlak, 2014a; Prasse, Wenk, Jasper, Ternes, & Sedlak, 2015). This results in limited oxygen diffusion to the inner parts, and the resulting oxygen gradient within the biofilm will allow both aerobic and anaerobic biodegradation (Jasper, Jones, Sharp, & Sedlak, 2014b).

3.3. CC removal mechanisms in a CW

3.3.1. Biodegradation

Aerobic and anaerobic biodegradation by microorganisms attached to the sediment and plants and present in biofilms is a key removal mechanism for CC in CWs. Parameters that determine the biodegradation efficiency in CWs are the presence of bacteria able to degrade the target contaminant, physicochemical properties of the contaminant of interest, its chemical structure and bioavailability, sediment composition, plant type, temperature, redox conditions, and organic matter availability (Faulwetter et al., 2009; Garcia-Rodríguez, Matamoros, Fontàs, & Salvadóó et al., 2014; Meng, Pei, Hu, Shao, & Li, 2014). High temperatures increase the microbial activity and thus the biodegradation in CWs (Huang, Cai, Zhong, & Wang, 2013; Wang & Li, 2015). Hence, the typical high CTBD temperatures of

±20 °C (Table 1) can improve a low biodegradation efficiency of CWs in countries with colder climates.

Many biocides can be biodegraded, including the most commonly used biocide glutaraldehyde (Campa et al., 2018; Kahrilas, Blotevogel, Corrin, & Borch, 2016; Kahrilas, Blotevogel, Stewart, & Borch, 2015; Laopaiboon, Phukoetphim, Vichitphan, & Laopaiboon, 2008; McLaughlin, Borch, & Blotevogel, 2016; Rogers, Ferrer, Tummings, Bielefeldt, & Ryan, 2017). Although biodegradation of a biocide sounds counterintuitive, biocides are biodegraded if their concentration is below the effect concentration or if the biocide does not target all microorganisms present. In addition, adsorption of glutaraldehyde to the sediment resulted in a decreased effective concentration and increased biodegradation (McLaughlin et al., 2016). Additionally, the formation of biofilms, as in surface flow CWs, has also shown to mitigate the negative effects of biocides by their protective functioning. Subsequently, biofilms play an important role in the biodegradation of high concentrations of biocides (Laopaiboon et al., 2008). Furthermore, autopolymerization of glutaraldehyde is believed to decrease its biocidal functioning (Kahrilas et al., 2016). Moreover, long-term exposure of microorganisms to glutaraldehyde alters the microbial community structure (Campa et al., 2018) and resulted in a higher resistance to this biocide, improving their potential for biodegradation (Vikram, Bomberger, & Bibby, 2015; Vikram, Lipus, & Bibby, 2014).

The microbial removal of surfactants, such as linear alkylbenzene sulfonates (LAS) and the main transformation products sulfophenyl carboxylates, was studied in horizontal subsurface CWs with various water depths (Huang et al., 2004). A shallow water depth allowing oxygen to enter the system and a high temperature had a positive impact on the LAS removal. Polyethylene glycol biodegradation was observed in soil inocula; however, its biodegradation was inhibited by the presence of glutaraldehyde (McLaughlin et al., 2016).

The biodegradation of corrosion and scale inhibitors, such as nitrite and phosphates, in CWs has been reviewed by various authors (Garcia et al., 2010; Lee, Fletcher, & Sun, 2009; Vymazal, 2007). The main processes responsible for the successful removal of nitrite in CWs are nitrification, denitrification and plant or microbial uptake (Lee et al., 2009; Vymazal, 2007). Microbial transformation is also an important removal mechanism for phosphates (Garcia et al., 2010). Currently, phosphate containing antiscalants are being replaced by non-phosphate antiscalants, such as polycarboxylic acids because of the negative impact of phosphates on the environment. Although different bacterial strains capable of degrading polycarboxylic acids have been isolated (Wen, Chen, Zhao, Zhang, & Feng, 2010), these CC are known to be resistant to biodegradation (Hasson,

Shemer, & Sher, 2011). Much effort is being put in the development of bio-based biodegradable antiscalants like glucose-based β-cyclodextrin-poly-ethylene glycol (Chauhan, Kumar, Kumar, Sharma, & Chauhan, 2012; Liu, Zou, Li, Lin, & Chen, 2016) and biodegradable co- and terpolymers with different functional groups (Bao, Li, & Zhang, 2016) which theoretically should be removed by microorganisms in CWs.

Benzotriazole and its derivatives are commonly used organic corrosion inhibitors in cooling towers and due to its omnipresence in surface waters globally, its environmental fate and biodegradability is well studied (Giger, Schaffner, & Kohler, 2006; Reemtsma, Miehe, Duennbier, & Jekel, 2010). The fate of benzotriazole in CWs has been subject of multiple studies resulting in conflicting removal efficiencies from 6% to 93% (Felis, Sochacki, & Magiera, 2016; Kahl et al., 2017; Matamoros, Jover, & Bayona, 2010; Matamoros, Rodriguez, & Albaiges, 2016; Matamoros, Rodriguez, & Bayona, 2017), which were attributed to different removal mechanisms. The CWs in the study by Matamoros et al. (2017) showed a benzotriazole removal of 9%. The CWs in that study are already functional for over 10 years. In contrast, higher benzotriazole removal rates were of >75% were found in the 5 year old traditional and intensified CWs in the study of Kahl et al. (2017), which were attributed to biodegradation. However, only comparing influent and effluent concentrations is not suitable for the determination of a removal pathway in a constructed wetland, given the fact that multiple removal pathways could play a role in benzotriazole removal. It is known that benzotriazole is taken up and transformed by plants (Castro, Davis, & Erickson, 2004), while benzotriazole has also shown to adsorb to sediments (Hart, Davis, Erickson, & Callender, 2004). Nevertheless, both the CWs in Kahl et al. (2017) and Matamoros et al. (2017) are planted with *Phragmites australis*, so the large difference in removal efficiency cannot be attributed to phytodegradation. A possible explanation could be that quick adaptation of the microbial community in the CWs in Kahl et al. (2017) resulted in higher biodegradation rates. In addition, the substrate in the latter CWs could have a higher adsorption affinity and/or capacity for benzotriazole.

3.3.2. Photodegradation

Direct and indirect photodegradation occurs in CWs with open water where sunlight can penetrate the water column. Direct photodegradation is the transformation of a contaminant as result of the absorption of sunlight. During indirect photodegradation, photoactive compounds, such as dissolved organic matter (DOM), nitrite and nitrate, produce radicals as result of the adsorption of sunlight, such as ^3DOM, $^{\bullet}OH$, $^1O_2$, and H_2O_2 (Page, Arnold, & McNeill, 2011). These radicals subsequently react with the

contaminant. Environmental parameters that influence the indirect and direct photodegradation of contaminants in CWs are (i) the presence of DOM, producing reactive species that enhance indirect photodegradation (de Laurentiis et al., 2014), but can also quench radicals, inhibiting indirect photodegradation (Wenk, Eustis, McNeill, & Canonica, 2013); (ii) the pH, influencing the formation of reactive oxygen species (Jasper & Sedlak, 2013); (iii) dissolved oxygen, quenching reactive species as ^{3}DOM (Brigante, Charbouillot, Vione, & Mailhot, 2010); and (iv) the water depth, determining light penetration (Alley, Willis, Rodgers, & Castle, 2013).

Several CC used in cooling towers are quickly removed by photodegradation. For instance, the commonly applied biocides 2,2-dibromo-3-nitrilopropionamide (DBNPA) and Bronopol show fast degradation as result of exposure to sunlight with 80% degradation of DBNPA within 72 h (Exner, Burk, & Kyriacou, 1973) and a 50% degradation in 70 h for Bronopol (Cui et al., 2011), respectively. Unfortunately, photodegradation of Bronopol results in the formation of 2-bromo-2-nitroethanol (BNE) and bromonitromethane (BNM), which are bioaccumulative and more persistent and toxic than the parent contaminant (Cui et al., 2011).

Various polymers used to prevent corrosion and scaling are photodegradable, such as polyacrylates (Kaczmarek, Kamińska, Światek, & Rabek, 1998) and phosphonates (Nowack, 2003; Lesueur, Pfeffer, & Fuerhacker, 2005. A half-life of 10–35 minutes was observed for the phosphonates diethylenetriaminepenta (methylenephosphonic acid) (DTPMP), nitrilotris (methylenephosphonic acid) (NTMP), hexamethylenediaminetetra (methylenephosphonic acid) (HDTMP), and ethylenediaminetetra (methylenephosphonic acid) (EDTMP) under middle pressure mercury lamps that were 125 times stronger than natural sunlight in the UV-B region (Lesueur et al., 2005). The presence of iron in CTBD could enhance the photodegradation rate of phosphonates (Lesueur et al., 2005). Formation of toxic transformation products also occurs during photodegradation of phosphonates (Nowack, 2003). This emphasizes the importance of identifying contaminant removal pathways in CWs instead of following the "black box system approach".

The corrosion inhibitor benzotriazole is susceptible to direct and indirect photodegradation, and various half-lives are reported in the literature. A half-life of 9 days was observed for direct photodegradation of benzotriazole (Weidauer, Davis, Raeke, Seiwert, & Reemtsma, 2016). Various methylated and oxygenated microbial transformation products of benzotriazole showed shorter half-lives of 2.5–5.2 days (Weidauer et al., 2016), indicating that a combination of biodegradation and photodegradation in a CW could increase its removal efficiency. Additionally, it was shown that the photodegradation half-life decreases

from 56.9 to 44.2 hours in river water containing DOM, as result of indirect photodegradation (Chung, Lin, & Lin, 2017). However, the same phenomenon was not observed for the methylated transformation product (Chung et al., 2017). The same study showed that benzotriazole acts as photostabilizer by hindering radical production, potentially decreasing the photodegradation efficiency of other photolabile compounds present in CTBD.

3.3.3. Adsorption

Adsorption to the sediment matrix, biofilms, and plants is an important removal mechanism in a CW. Adsorption is determined by several properties of the contaminant itself, including its chemical structure, water solubility, and acid/base properties. Furthermore, environmental parameters, such as redox potential, pH, temperature, ionic strength, the presence of divalent, and trivalent cations and the composition of the soil organic matter, play an important role in adsorption processes (Bui & Choi, 2010). Various adsorption mechanisms, such as van der Waals interaction, electrostatic interaction, ion exchange, surface complexation, and hydrophobic partitioning, result in the adsorption of contaminants to the CW substrate's mineral surface, organic carbon, plant roots and biofilms (Li et al., 2014; Wu, Zhang et al., 2015; Zhang et al., 2014).

Sorption of a contaminant does not transform a contaminant but removes it from the water phase, whereas microbial degradation and photodegradation lead to the formation of transformation products and potential mineralization. This removal from the water phase can also have a negative consequence, since the contaminant might be desorbed and become bioavailable at later stages. In addition, contaminants can accumulate in the CW matrix, requiring treatment of the matrix eventually. However, adsorption also allows a longer contact time between contaminants and microorganisms present at the sorbents surface which consequently may favor microbial degradation (Lin, Lin, Tung, & Chary, 2010; Weissenfels, Klewer, & Langhoff, 1992).

A commonly used parameter to predict adsorption of a contaminant in CWs is the n-octanol/water partition coefficient ($\log K_{ow}$) predicting low adsorption for contaminants with a $\log K_{ow} < 3$ (Hijosa-Valsero, Matamoros, Martín-Villacorta, Bécares, & Bayona, 2010; Matamoros, Arias, Brix, & Bayona, 2007). Inherent to their functioning as CC, most biocides and corrosion inhibitors are hydrophilic contaminants that have a $\log K_{ow}$ in the range of −1 to 2 (see Table 2), indicating that these contaminants do not tend to adsorb to the CW substrate. Nevertheless, significant adsorption of glutaraldehyde ($\log K_{ow} = -0.18$) of 23–40% to a sandy loam sediment with a TOC content of 7.9 g/kg occurred in biological removal

tests, and this adsorption decreased the inhibiting effect of glutaraldehyde on microorganisms activity resulting in subsequent biodegradation (McLaughlin et al., 2016). This shows that it is difficult to predict the adsorption of a contaminant on the basis of parameters as the log K_{ow} only, because of the different adsorption mechanisms occurring and the previously mentioned characteristics of the substrate and the contaminant itself (Goss & Schwarzenbach, 2001; Zhang et al., 2014).

Antiscalants form complexes with minerals and thus show high sorption tendencies. Phosphates and phosphonates adsorb strongly to clay minerals, such as goethite (Garcia et al., 2010; Nowack & Stone, 2006). Iron-coated sand has been studied for its adsorption and subsequent recovery of common phosphonate antiscalant NTMP from reverse osmosis concentrate and has shown to be a cheap and promising filtration medium (Boels, Keesman, & Witkamp, 2012; Boels, Tervahauta, & Witkamp, 2010). This iron-coated sand could be used in CWs as well.

Adsorption is an important removal pathway for inorganic corrosion inhibitors, such as zinc (Gillespie, Hawkins, Rodgers, Cano, & Dorn, 2000; Yang et al., 2006). It was shown that 97% of the zinc that was removed by a horizontal subsurface flow CW was bound to an alluvial floodplain substrate (Gillespie et al., 2000). Organic corrosion inhibitors, such as benzotriazole, also adsorb to the sediment (Hart et al., 2004). However, the sorption of benzotriazole to the sediment is heavily influenced by the pH (Hart et al., 2004). At higher pH, close to its pK_a of 8.3, benzotriazole sorption was 50% lower than at a pH of 6 (Hart et al., 2004). Since the CTBD generally has a slightly neutral pH (see Table 1), this could negatively affect the adsorption of benzotriazoles.

Adsorption has also shown to be an important pathway for surfactant removal. A LAS removal of 30% in a surface flow CW, 56% in a subsurface flow CW and 41% in a gravel filter was mainly attributed to adsorption to the sediment matrix (Fountoulakis, Terzakis, Kalogerakis, & Manios, 2009).

3.3.4. Plant uptake

The plants in CWs fulfill various purposes. Plants can directly remove contaminants by actively taking them up in their biomass, accumulating them and enzymatically breaking them down (He et al., 2017; Hurtado et al., 2016; Malchi, Maor, Tadmor, Shenker, & Chefetz, 2014). Plants also indirectly influence the removal of components by excreting exudates, nutrients and oxygen for microorganisms in the rhizosphere, thus stimulating microbial degradation (Garcia et al., 2010; Zhai, Piwpuan, Arias, Headley, & Brix, 2013).

The choice of plants species influences the contaminant uptake by plants and input of oxygen and root exudates in the CW (Brisson & Chazarenc,

2009; Leto, Tuttolomondo, La Bella, Leone, & Licata, 2013; Vymazal, 2011). Few studies have been performed on the uptake of CC by plant species. An exception is the uptake of metals, such as zinc, that is accumulated by common CW plants as *Phragmites australis* (Liu, Dong, Xu, Wang, & Xu, 2007; Peverly, Surface, & Wang, 1995). The tendency of an organic contaminant to be taken up by plants is affected by the component's lipophilic nature (Imfeld et al., 2009). Generally, contaminants with a log $K_{ow} > 4$ are less taken up by plants (Imfeld et al., 2009). The phytoremediation of benzotriazoles (log $K_{ow} = 1.44$) by sunflowers (*Helianthus annuus*) was studied and benzotriazoles were actively taken up and transformed by the plants when the concentration of benzotriazoles was lower than the toxic threshold of 100 mg/L (Castro, Davis, & Erickson, 2003; Castro et al., 2004). As a follow up the application of horizontal flow CWs planted with *Phragmites* spp., *Typha latifolia*, and *Schloenoplectus lacustris* for the removal of benzotriazoles was studied and an increased removal in the planted CWs was observed (Castro, Davis, & Erickson, 2005). In contrast, the removal of benzotriazole in unplanted vertical flow CWs and similar CWs planted with *Phalaris arundinacea* var. *picta* L. was studied and no difference in removal efficiency between the two was observed (Felis et al., 2016).

The uptake of other emerging contaminants as pharmaceuticals with different log K_{ow} in CW plants *Phragmites australis* and *Typha angustifolia* was studied and uptake of contaminants was observed with a log K_{ow} both lower and significantly higher than 4 (Hijosa-Valsero, Reyes-Contreras, Domínguez, Bécares, & Bayona, 2016). Petrie et al. (2018) observed uptake of emerging contaminants with a low K_{ow} in *Phragmites australis,* such as caffeine (log $K_{ow} = 0.16$), while atenolol (log $K_{ow} = 0.03$) was not taken up. It was hypothesized that this behavior is governed by the charge of the chemical, because negatively charged chemicals are repulsed by the negatively charged membranes of the plant roots (Petrie et al., 2018). Hence, CC that is negatively charged in the CTBD will likely not be taken up by the plants.

In conclusion, it is not unambiguously shown that the incorporation of plants in CW is beneficial for the removal of CC. Hence, more research is needed to the tendency of the hydrophilic and hydrophobic CC with different charges to be taken up and transformed by plants.

4. Potential limitations of CW treatment prior to desalination

Different components in the CTBD have the potential to hinder the optimal removal of CC prior to physicochemical desalination. In addition, various compounds can be formed in the CW that can subsequently influence the physicochemical desalination process.

4.1. The salinity of the cooling tower water

CTBD has a moderate EC of 1500–4000 μS/cm (Table 1). The salinity of CTBD can have multiple effects on the functioning of CWs with respect to contaminant removal. Increasing water salinities have a negative effect on the biodegradation efficiency (Lefebvre & Moletta, 2006). Furthermore, high salt concentrations have an adverse effect on the sorption of cationic CC to the soil matrix, since both CC and salt ions compete for the same ion-exchange sites (Kahrilas et al., 2015). In addition, CWs fed with saline wastewater require salt tolerant plant species (Klomjek & Nitisoravut, 2005).

Various authors studied the effect of the salinity on the treatment performance of CWs. For instance, a horizontal subsurface flow CW planted with *Arundo donax* and *Sarcocornia fruticosa* removed 51–80% COD and 53–90% BOD_5 from a saline industrial wastewater (Calheiros et al., 2012). No changes in the EC of ±17000 μS/cm occurred as result of the CW treatment. The influence of an average EC of 15000 μS/cm on the removal efficiency of CWs planted with eight different plants was studied and the highest removal rate for general water quality parameters, such as BOD_5 and TSS, was found for *Digitaria bicornis* (Klomjek & Nitisoravut, 2005). The influence of different salinities on the removal of the herbicide atrazine was studied and an exponential removal inhibition by higher salinities as result of a shift in the microbial population was shown (Lin et al., 2008). Although CWs seem to cope with saline wastewaters according to their removal performance for general water quality parameters, little research has been conducted on the influence of the salinity on the removal of micropollutants. Hence, further research to the influence of salts on the removal of the CC is required.

Phytodesalination is a recently described CW mechanism that could decrease the costs and energy demands associated with physicochemical desalination technologies. Phytodesalination is the uptake of salts by salt tolerant plants, halophytes, which reduces the salinity of saline water streams. The phytodesalination capability of salt tolerant plant species *Bassia indica* in a vertical flow CW showed a 12–60% EC decrease of an initial EC of 1000–16000 μS/cm as result of accumulation of ions in the plant leaves (Shelef, Gross, & Rachmilevitch, 2012). Higher salt removal rates were found for the experiments with a low starting EC. However, employing phytodesalination seems limited to regions with moderate climates. A study on phytodesalination by *Bassia indica* in a horizontal flow CW under hot arid conditions indicated that the plants did take up significant amounts of Na^+ ions. This uptake did not result in a decreased salinity of the effluent water due to strong evapotranspiration (Freedman, Gross, Shelef, Rachmilevitch, & Arnon, 2014). Many recent studies are

searching for new halophytes that take up salts without losing their ability for the uptake of nutrients and heavy metals (Fountoulakis, Sabathianakis, Kritsotakis, Kabourakis, & Manios, 2017; Jesus, Cassoni, Danko, Fiúza, & Borges, 2017).

4.2. Toxicological effects of CC in the CW

The input of potentially toxic contaminants in the CW that can be entered by avian and aquatic animal species requires a proper ecotoxicological risk assessment to prevent unwanted environmental effects. In addition, CC removal as result of microbial degradation is an important aspect of the CW functioning that could be hampered by the input of toxic chemicals. Glutaraldehyde has shown to inhibit biodegradation of various chemicals by an aquifer sediment inoculum (Rogers et al., 2017). Since the type of CC and their concentrations are known by the water treatment facilitator, specific (mixtures of) contaminants can be subjected to different toxicological tests to determine their short- and long-term toxicological effect.

The toxic effects of biocides are well documented, due to worldwide legislation that demands proper toxicological testing of newly developed biocides before their market introduction. Due to its biocidal functioning, the toxicity of a biocide is an important parameter when exposing CW systems to these contaminants. Kahrilas et al. (2015) gave an overview of the toxicity of biocides used in hydraulic fracturing. Many of these biocides are similar to those used in cooling tower systems. For both applications, glutaraldehyde and DBNPA are the most commonly used biocides. Both biocides show 50% mortality (LC_{50}) in the mg/L concentration range for different aquatic organisms (Kahrilas et al., 2015), which is in the same order of magnitude as their discharge concentrations and thus could significantly influence the CW's biological functioning.

Studies of the toxicity of metals used as corrosion inhibitor are common. Zinc has shown to have toxic effects to waterflea *Daphnia magna* in concentrations above 250 μg/L (Muyssen, de Schamphelaere, & Janssen, 2006). Chromate at concentration levels similar to those common in CTBD results in significant growth inhibition of aqueous vegetation duckweed (*Lemna minor*) (Appenroth, Luther, Jetschke, & Gabrys, 2008). Organic corrosion inhibitors could also pose a threat to the CW. The ecotoxicological effects of benzotriazole have been extensively studied (Alotaibi, McKinley, Patterson, & Reeder, 2015; Seeland, Oetken, Kiss, Fries, & Oehlmann, 2012), since it is widely used and found in the aquatic environment. EC_{10} (concentration where 10% of the organisms are affected) values of 1.18, 3.94, and 79.7 mg/L, have been reported during acute 48 h tests for freshwater algae (*Desmodesmus subspicatus*), *Lemna minor*, and *Daphnia magna*,

respectively (Seeland et al., 2012). Benzotriazole is often present in CTBD in the low mg/L range.

Toxicity assessments of new antiscalant formulations are less frequently carried out, although the environmental impact is a main driver in their development. In addition, the development of proprietary CC with unknown formulation hampers a complete understanding of their environmental fate. For instance, the toxicity of a RO concentrate with and without an antiscalant with unknown formulation was tested on freshwater crustaceae *Gammaris pulex* and *Gammaris roeseli* (Feiner, Beggel, Jaeger, & Geist, 2015). In this study, the pure concentrate did not show any toxicological effects. On the other hand, the addition of the antiscalants resulted in an increased mortality with an EC_{50} concentration for the antiscalants containing concentrate of 4–8.7 mg/L, likely as a result of synergistic toxicity effects between the antiscalant and the concentrate (Feiner et al., 2015). Hence, the removal of antiscalants by CW prior to RO does not only improve the RO efficiency but can also significantly decrease toxicity of the solution.

The toxicity of CC is not always caused by the parent contaminant, but can also be caused by its transformation products. As mentioned earlier, the degradation of biocides can lead to the formation of transformation products that are more toxic and persistent than the parent contaminant (Lesueur et al., 2005; Cui et al., 2011). In addition, toxic byproducts can be formed as result of mutual interaction of the CC. Simultaneous biodegradation of biocide glutaraldehyde and antiscalant polyacrylamide showed that the reactive aldehyde groups forms bonds with the amine group of the polyacrylamide. It was speculated that these products retained some biocidal functioning (McLaughlin et al., 2016). As a result, chemical analysis may reveal the absence of toxic glutaraldehyde, while a toxic effect may still be observed. Proper environmental fate assessment including mass balance calculations for the used CC is thus critical for sustainable use of these CC and their removal in CW.

4.3. Formation of byproducts in CWs

CWs remove COD, N and P as well as various CC from waste water streams. However, possible forms of contamination that could hinder subsequent desalination of the water can be produced *in situ* in CWs. The dissolved organic carbon (DOC) concentration in a newly started surface flow CW was monitored and an increase in concentration in the effluent was observed, which was attributed to DOC leaching from plants (Scholz et al., 2016). In addition, when the biopolymer composition in surface flow CWs with different plants used as polishing step for conventional waste water

treatment was studied it was found that the DOC in CWs with *Typha* increased by 140% in summer as result of leaching by decaying plants (Chon, Park, & Cho, 2013). Furthermore, the DOC became more hydrophobic and had a larger molecular weight, which is the result of humification of the waste water treatment effluent DOC (Chon et al., 2013). Humic substances have been shown to cause fouling of membranes and in this way influence functioning of the membranes similar to CC (Xie, Nghiem, Price, & Elimelech, 2013). This would significantly impact subsequent desalination steps.

In many CTBD streams, residual free chlorine used as biocide is present. In addition, biocides, such as DBNPA, release bromide ions. These halogens can react with (newly formed) natural organic matter (NOM) after discharge in CWs, resulting in the formation of disinfection byproducts (DBP), such as trihalomethanes (THM), some of which are carcinogenic (Chow, Tanji, & Gao, 2003; Gallard & von Gunten, 2002). Apart from being toxic, THM affect membrane separation properties (Karakulski, Gryta, & Morawski, 2001), and this way have a negative impact on physicochemical desalination.

5. CW design considerations

The installation of a CW for CTBD pretreatment requires thorough research into its design to function optimally, to avoid problems with toxic CC and to prevent the production of compounds that have the potential to hamper physicochemical desalination. In addition, the construction of CWs requires space and a cost-analysis for the installation, energy and maintenance costs of a CW. These are, however, beyond the scope of this review, since these are often case-specific. Furthermore, several practical design parameters, such as the type of water flow and the hydraulic retention time should be considered.

The water flow type determines the dominating removal mechanisms that occur (paragraph 3.2). Previous paragraphs have outlined that the different classes of CC (paragraph 2) can be removed by different removal mechanisms in the CW (paragraphs 3.3.1–3.3.4). Hence, a combination of different water flow types, that is removal mechanisms in a 'hybrid' CW sequence (Figure 2) gives the highest removal efficiency for the total cocktail of different CC.

The hydraulic retention time (HRT) is an important design parameter that influences the removal efficiency of CWs (Akratos & Tsihrintzis, 2007; Ghosh & Gopal, 2010; Toet, Logtestijn, Kampf, Schreijer, & Verhoeven, 2005). The HRT defines the contact time between the CC and the sediment matrix including its microbial community in a subsurface flow CW or the illumination time in a surface flow CW. A retention time of 4 days instead

of 1 day increases the removal efficiency of CWs for bulk pollutants as COD and TN and the stability thereof (Ghosh & Gopal, 2010). However, higher retention times require large CWs in terms of space or low inflow rates. Low inflow rates might be unrealistic considering the generally large volumes of CTBD discharged by cooling towers. Another important design parameter is the hydraulic loading rate, which determines the quantity of CC to be removed and the potential saturation time of the CW substrate (Ávila, Matamoros et al., 2014, Carballeira, Ruiz, & Soto, 2016). This is especially relevant for substrates with a high adsorption capacity that lose their function once saturated.

Several technical measures have been studied to improve the efficiency of the different removal mechanisms in the CWs with different water flow types. Biodegradation is an important removal mechanism for all classes of CC and thus should be stimulated. Possible measures to increase the biodegradation of CC in CWs were reviewed recently (Meng et al., 2014). Examples are aeration, artificial substrates, bioaugmentation and varying redox conditions, in the form of sequential CW systems. Aeration increases the aerobic biodegradation of pharmaceuticals from a hospital wastewater (Auvinen et al., 2017), while multiple redox conditions allow both aerobic and anaerobic biodegradation. Bioaugmentation is the addition of microorganisms known to degrade certain contaminants to a CW. However, in order to successfully bioaugment CWs, extensive research is needed on the microbial communities responsible for the degradation of the specific contaminants, in order to evaluate their long term survival, adaptation and performance in CW systems under alternating conditions (Cycoń, Mrozik, & Piotrowska-Seget, 2017; Meng et al., 2014).

Adsorption has been shown to be an important removal mechanism for antiscalants and corrosion inhibitors. The CW substrate composition defines the adsorption capacity of the CW (Ge et al., 2015; Sakadevan & Bavor, 1998). Wu et al. (2015) recently published an overview of commonly used substrates to enhance adsorption processes in CWs, such as natural clay minerals, industrial by-products and activated carbon. The incorporation of such substrates in a CW for enhanced adsorption of CC is an interesting option, given the importance of the adsorption process in a CW and the variety of adsorption substrates studied. This substrate could either be used as stand-alone substrate (Bruch et al., 2011) or mixed with a sandy substrate (Prochaska & Zouboulis, 2006). The amendment with enhanced adsorption substrates, for instance by mixing sand with iron-coated sand, is especially interesting for vertical flow CWs because of the smaller space requirements, which makes it economically feasible and provides the possibility of installing multiple adsorption layers on top of each other (Nakamura et al., 2017).

During the last decade, many studies focused on the removal efficiency of enhanced photodegradation, i.e. photocatalysis, of various emerging contaminants in natural water matrices. These studies reported high removal rates for pharmaceuticals and pesticides (He, Sutton, Rijnaarts, & Langenhoff, 2016; Prieto-Rodriguez et al., 2012; Quiñones, Rey, Álvarez, Beltrán, & Li Puma, 2015). Lab-scale combinations of subsurface flow CWs and photocatalysis were successful in the removal of these contaminants as well. A combination of lab-scale planted and unplanted vertical flow CW columns with TiO_2 photocatalysis resulted in a removal of 83% of benzotriazole for the CW, while the combination of the CW and photocatalysis resulted in a removal of 96% (Felis et al., 2016). However, the photocatalysis occurred in reactors of 350 ml (Felis et al., 2016). The extrapolation of these successful lab-scale studies to full scale CWs has not been performed. Enhanced photodegradation on the CW scale could significantly improve the removal of CC from CTBD, but requires additional research on the energy requirements, sustainability, and environmental fate of the catalysts used.

Combinations of CW designs could be beneficial for the overall CW functioning. The toxicity of CTBD and the production of toxic transformation products could pose a threat to the microbial communities responsible for biodegradation. Hence, the abiotic removal of biocides in surface flow CWs prior to subsurface flow CWs in which biodegradation is an important removal mechanism could increase the total biodegradation efficiency. Additionally, subsurface flow CWs could be equipped with a substrate layer with enhanced adsorption capacity, such as biochar, activated carbon or iron-coated sand, to remove potentially harmful CC before they come into contact with microorganisms. In addition, a high adsorption capacity substrate in the last step of a hybrid CW system could be used for the adsorption of DOC and byproducts produced *in situ*.

6. Concluding remarks

- CWs can remove CC from CTBD, and this way increase physicochemical desalination efficiency. In addition, CWs can contribute to CTBD desalination itself.
- The most important removal mechanisms for CC in a constructed wetland are adsorption, aerobic and anaerobic biodegradation, photodegradation, and uptake by plants.
- The dominant conditioning chemical removal mechanisms in a constructed wetland are determined by its water flow type. Due to the variety of CC used in cooling towers, a combination of multiple CWs with

different water flow types facilitating various removal mechanisms is the best solution for the treatment of CTBD.

- It is of utmost importance to determine and monitor the exact removal mechanism of CC, since transformation products and by-products might be more harmful than the parent compounds to both the constructed wetland and subsequent physicochemical treatment technologies.
- An assessment of environmental risks and treatability of various newly produced antiscaling polymers used in cooling towers is lacking. In addition, the development of new proprietary polymers by water treatment companies without publishing full product description leads to difficulties in (i) developing adequate analytical techniques; (ii) technical testing of the treatability of water containing these compounds; and (iii) evaluation and assessment of their environmental fate.

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