UNIVERSITEIT VAN AMSTERDAM

Removal and Transformation of Conditioning Chemicals in Constructed Wetlands Treating Cooling Tower Water

T.V. Wagner

Summary

This thesis describes the removal and transformation of conditioning chemicals in constructed wetlands treating cooling tower water.

The application of constructed wetlands to lower the fresh water footprint of cooling towers in delta areas is introduced in **chapter 1**. Delta areas worldwide are threatened by fresh water scarcity as a result of a rising demand for fresh water for food production, drinking water, public hygiene and industrial production. In addition, the supply of fresh water is jeopardized by climate change and the intrusion of salt water. Therefore, the NWO-TTW research program Water Nexus aims to evoke a paradigm shift in water sourcing and use in delta areas: Saline waste water is no longer considered as a threat but as a valuable resource that can reused, which lowers the pressure on fresh water sources. Hence the slogan of Water Nexus is: '*Saline water where possible, fresh water where essential*.'

Large producers of saline waste water are industrial cooling towers. To produce this large volume of saline waste waters, cooling towers take up large volumes of fresh water for their cooling processes, which makes them the most substantial contributor to the industrial fresh water uptake. The fresh water footprint of cooling towers can be lowered by reusing the saline discharged cooling tower water, cooling tower blowdown (CTBD), in the cooling tower as 'make-up' water. Therefore, the CTBD requires desalination. The Water Nexus research program studies the possibility for this reuse using the cooling towers of the Dow ELSTA facilities in Terneuzen as a case study. These cooling towers use fresh water from remote sources, and the reuse of their own CTBD would significantly lower their dependency of remote fresh water sources and guarantee the supply of fresh water during periods with less fresh water supply, such as droughts. The aim of the Water Nexus program is to develop an integrated treatment train of green and grey technologies that allow the reuse of this CTBD. Grey treatment technologies allow the desalination of the CTBD. A central part of this treatment train is reserved for green treatment technologies in the form of constructed wetlands (CWs).

CWs are man-made wetland systems in which natural processes, such as biodegradation, photodegradation, plant uptake and adsorption remove contaminants from the water. These CWs can function as a pre-treatment before desalination to remove fractions from the CTBD that could hamper its desalination, such as PO_4^{3-}, NO_3^-, total suspended solids (TSS) and conditioning chemicals (CCs). CCs are added to the cooling tower to prevent processes, such as scaling, fouling and corrosion. However, CCs, and the earlier mentioned fractions, cause for instance fouling of membranes of physico-chemical desalination technologies, which results in a decreasing desalination efficiency and increasing energy consumption. Hence, the main objective of the research in this thesis are i) to study the removal and transformation of CCs in CWs; ii) to study the toxic effect of CCs in and on the CW and iii) to determine the most optimal CW system for the treatment of CTBD before its desalination.

The current state of knowledge about the removal of CCs in CWs is reviewed In **chapter 2**. First, an overview of commonly used CCs in cooling tower water, such as antiscalants, corrosion inhibitors, biocides and biosurfactants, is provided. Subsequently, the functioning of a CW is elucidated and the importance of the CW design, that determines the efficiency of removal mechanisms is highlighted, such as biodegradation, adsorption and plant uptake. The efficiency of these removal mechanisms for the different classes of CCs is discussed and potential threats for proper functioning of these mechanisms are identified. The review finishes with recommendation for the design of a CW for CTBD treatment, and provides technological solutions to overcome earlier identified threats to proper CW functioning.

The removal of corrosion inhibitor benzotriazole in pilot-scale CWs and batch removal experiments is studied in **chapter 3** to i) elucidate important removal mechanisms for benzotriazole from CTBD in CWs and ii) to examine the applicability of performing batch removal experiments with material from CWs to predict the removal efficiency of CWs. Knowledge on the relevant removal mechanisms of a CC allow the tailor-made design of a CW for optimal removal of a given CC. The removal of benzotriazole in horizontal subsurface-flow CWs (HSSF-

CWs), vertical subsurface flow-CWs (VSSF-CWs) and surface-flow CWs (SF-CWs) was determined. Material from these CWs was used to perform batch biodegradation and adsorption experiments. Adsorption contributed the most to benzotriazole removal, according to the removal rates obtained in batch removal experiments. The removal of benzotriazole was the highest in the VSSF-CW as result of the aerobic redox conditions in the VSSF-CW that allow aerobic biodegradation. Performing batch removal experiments did provide insights in the relevant removal mechanisms for benzotriazole in CW. However, it was not possible to predict the removal efficiency of a CW by performing batch experiments, probably because these experiments underestimate the biodegradation capacity of the microbial community.

The impact of the biocides DBNPA and glutaraldehyde on the biodegradation of the corrosion inhibitor benzoic acid by CW microorganisms is assessed in **chapter 4**. Benzoic acid was inoculated with concentrations of the biocides that are relevant in practice, and DBNPA had a stronger negative effect than glutaraldehyde on the required time for complete benzoic acid biodegradation. This implies that biodegradation in CWs can be hampered by the biocides in CTBD. Surprisingly, the negative effect on the biodegradation of benzoic acid of DBNPA combined with glutaraldehyde was lower than the effect of DBNPA alone. Non-target screening combined with the data processing workflow 'patRoon' was used to elucidate the mechanisms behind the antagonistic toxic effect of DBNPA plus glutaraldehyde. It was observed that glutaraldehyde increased the transformation rate of DBNPA to the newly discovered transformation product 2,2-dibromopropanediamide. In addition, DBNPA and glutaraldehyde formed new transformation products as result of mutual interaction, and these products are probably less toxic than DBNPA itself. Since it is the first time that these products are observed, their fate in both the cooling tower and the CW is not known yet.

The influence of photodegradation in a SF-CW on the toxicity of DBNPA in CTBD is assessed in **chapter 5**. The toxicity of DBNPA in CTBD in SF-CWs is relevant because local fauna can enter this type of CW. DBNPA in CTBD was exposed to simulated sunlight, and samples were taken for transformation product determination by non-target analysis combined with the data processing workflow 'patRoon' and *Daphnia magna* 48 h acute toxicity tests. The toxicity of DBNPA in CTBD was lower than toxicity values reported in the literature for this chemical in other solution, and non-target screening showed that this was due to complete DBNPA transformation within hours. This transformation probably occurred via MBNPA and NPA. Photodegradation resulted in an increased DBNPA toxicity after 1 h of illumination as a result of the production of DBNPA photodegradation products. An increased toxicity as a result of photodegradation was not observed after 48 h and 96 h of illumination. The interaction with glutaraldehyde resulted in the formation of interaction products, although this formation did not alter the toxicity of DBNPA. Photodegradation did not result in the formation of unique interaction products, but did impact the interaction product behaviour over time. Because of the observed toxic effect of DBNPA in CTBD, it is not recommended to use a SF-CW as the first treatment step of a hybrid-CW for CTBD treatment.

The integration of a lab-scale VSSF-CW with electrochemical oxidation (EO) by a boron-doped diamond (BDD) or mixed-metal oxide (MMO) anode and vice versa for the removal of organic chemicals (OCs) and benzotriazole from CTBD is studied in **chapter 6**. Direct CTBD treatment by the VSSF-CW did not result in substantial OCs removal, because the OCs mainly consisted of recalcitrant humic acids. Benzotriazole was almost completely removed in the VSSF-CW. Subsequent EO of the VSSF-CW effluent resulted in almost complete OCs removal, but produced effluent that was toxic to *Vibrio Fischeri* as a result of the production of organic and inorganic chlorinated compounds. Direct CTBD treatment by EO resulted in substantial OCs and benzotriazole removal. Subsequent treatment by VSSF-CWs did not result in additional OCs removal. In addition, the Phragmites australis in the VSSF-CWs died, as a result of the production of organic and inorganic chlorinated compounds. This production also resulted in a final effluent that was highly toxic to *Vibrio Fischeri*. Treatment of the toxic EO-effluent in the VSSF-CWs did result in a decrease of the toxicity of the CTBD. Before integrating VSSF-CWs with EO, it is recommended to identify how to mitigate the toxic effect of EO byproducts.

The application of hybrid-CWs for the treatment of CTBD is assessed in **chapter 7**. Six hybrid-CWs, consisting of a HSSF-CW, VSSF-CW and a SF-CW combination, were fed with synthetic CTBD. The objective of this study was to determine i) the baseline removal efficiency for CTBD compounds that hinder physico-chemical desalination during summer; ii) the dominant removal mechanisms for these fractions; iii) the effect of winter season on the baseline removal efficiency; iv) the effect of biocides on the baseline removal efficiency; v) the most optimal order of different CW flow types within a hybrid-CW. The hybrid-CWs were able to remove fractions that hamper physico-chemical desalination technologies, such as PO_4^{3-}, NO_3^-, TSS, TOC and benzotriazole and benzoic acid. Benzotriazole, benzoic acid and NO_3^- were removed by biological removal mechanisms, whereas PO_4^{3-}, TSS and TOC were removed abiotically. Benzotriazole biodegradation requires aerobic redox conditions in the VSSF-CW, whereas NO_3^- denitrification requires anaerobic redox conditions in the HSSF-CW. The removal efficiency of the biological removal mechanisms was negatively impacted by winter season, but was not affected by the addition of biocides in concentrations that are relevant for practice. For optimal pre-treatment of CTBD before desalination, a hybrid-CW starting with a VSSF-CW followed by a HSSF-CW is recommended. An SF-CW is not required for pre-treatment of the CTBD, but does allow the storage of large volumes of water and development of a natural ecosystem. When applied, this flow type should be in between the VSSF-CW and HSSF-CW as a second treatment stage.

The findings of chapter 2 to chapter 7 are used to discuss the pathway towards the construction of full-scale CWs for the treatment of CTBD in **chapter 8**. An overview of commonly used design tools to calculate the dimension of a full-scale CW is provided. In addition, tools to predict the removal efficiency of a CW for a given compound are introduced. Subsequently, important design parameters, such as the hydraulic retention time, loading rate, substrate, vegetation and water depth, are discussed. Afterwards, practical design consideration for the design of a full-scale CW are provided and monitoring options are suggested. Then, an overview of technological solutions to improve the removal efficiency of CWs treating CTBD is provided and the impact of CW treatment on the functioning of physico-chemical desalination technologies is discussed. Chapter 8 finishes with an overview of additional benefits of using full-scale CWs for the treatment of CTBD and the identification of future research directions prior to installing these full-scale CWs.