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Characterization of the organic micropollutants behavior during electrochemical ammonia recovery

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ABSTRACT

Nutrient recovery systems can be impacted due to the presence of organic micropollutants (OMPs). TAN (total ammonium nitrogen, sum of ammonium and ammonia) recovery from wastewater can be achieved by combining an electrochemical system with membrane stripping. Essential components of these processes are cation-exchange membranes and a hydrophobic gas-permeable membrane. These membranes are barriers between the OMPs source (wastewater) and recovered products. Despite reports about OMPs – ion exchange membrane interactions, there is limited knowledge about the transport of OMPs in ammonium recovery systems. This work gives a first detailed description of the transport mechanism of a broad group of OMPs with varying properties during electrochemical ammonium recovery supplied with a complex matrix (digested blackwater). Even after continuous exposure to OMPs and consequent system equilibration, OMP concentrations in the effluent were often lower than in the inflow stream. The highest removal and transport towards the concentrate were found for positively charged OMPs. The presence of organic matter contributed to the adsorption and transport of OMPs. Although OMPs were transported over the CEMs, the gas permeable hydrophobic membrane for ammonia recovery retained all OMPs.

1. Introduction

The presence of organic micropollutants (OMPs) in diverse ecosystems is a direct consequence of the growing consumption of a vast amount of chemicals. OMPs comprise a broad spectrum of daily-used products, e.g., pharmaceuticals, pesticides, personal care products, and plasticizers. The global occurrence of OMPs in different water resources has raised a serious concern about their harmful effects on aquatic ecosystems and human health, and numerous investigations have reported their environmental hazard [35,37,43,54]. OMPs removal from aqueous (waste) streams has already been studied using several water treatment technologies, e.g., advanced oxidation processes [52,70] and activated carbon adsorption [17,71]. It has been shown that OMPs removal in those technologies largely depends on the physicochemical properties of OMPs [22]. As OMPs are characterized by an enormous variety of physicochemical properties, an effective solution to remove all OMPs from waste streams does not exist. Wastewater treatment plants (WWTP) are not designed to remove OMPs, thus OMPs are present in their effluents, in concentration ranges from ng L^{-1} up to µg L^{-1}. Consequently, OMPs are continuously being introduced into the aquatic environment [9,15,20,24–26,36,39,56,58,64,65].

Wastewater is more and more regarded as an important resource stream containing nitrogen, among other valuable nutrients. The current state-of-the-art technology in WWTPs to avoid nitrogen accumulation in

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Abbreviations: BW, digested black water; CEM, cation exchange membrane; COD, Chemical oxygen demand; DD, Donnan dialysis; ED, Electrodialysis; ES, electrochemical system; IEM, ion exchange membrane; LLMC, liquid/liquid membrane contactor; MEA, membrane electrode assembly; MRM, multiple reaction monitoring; OMP, organic micropollutant; SBW, Synthetic black water; TAN, total ammonium nitrogen, sum of ammonium and ammonia.

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water bodies is nitrogen removal by the nitrification/denitrification process or Anammox process [28,48,61]. Both processes convert reactive nitrogen into its inert gas form (N_2), which is lost to the atmosphere [59]. However, it has become important to develop more sustainable technologies capable of recovering the reactive nitrogen present in wastewater [2,8,13,29,31]. TAN (total ammonium nitrogen, sum of ammonium and ammonia) recovery using ion exchange membranes/electrodialysis was previously demonstrated as an efficient process in regards to TAN recovery and energy consumption [13,19,21,27,30,34,48,49,60]. However, when recovering a nutrient, the OMPs presence in wastewater might become an issue for the acceptance of the product and hence the nutrient recovery technology.

To prevent the further spreading of OMPs in the environment, it is essential to investigate the transport and adsorption of OMPs in membrane technologies [4,10,12]. Reverse osmosis and nanofiltration have been reported as the most efficient technologies for OMPs removal from waste streams [7,32,40,69]. However, despite its importance, as electrodialysis (ED) showed irregular removal of OMPs, the behavior of OMPs in ED has received limited attention [4,55]. Available research reports electrochemical systems (ES) as a technology that has the potential to separate some OMPs from nutrients found in urine since the mobility of OMPs in ion exchange membranes (IEMs) is lower than the mobility of other ions like NH_4^+, PO_4^{3-} and K^+ [4,41,66]. Other studies focused on the production of OMPs-free fertilizer either by ammonia stripping, which was unsuccessful [8], or by coupling an electrochemical cell with a membrane stripping system [13]. The fertilizer produced by coupling an electrochemical cell with a membrane stripping system was OMPs-free, but only six OMPs were tested. Nevertheless, the need to verify these findings in a complex matrix was indicated, and a larger number of OMPs with varying in properties (e.g., charge, size, and hydrophobicity) should be studied to make ES a safe ammonia recovery process. Further insights into the OMP transport mechanisms under the specific conditions during electrochemical ammonia recovery are needed.

This work aims to investigate the transport mechanism of OMPs over the CEMs during continuous electrochemical ammonium recovery from a complex matrix such as digested black water. This is the first study providing an in-depth description of the transport and adsorption of OMPs to CEMs simultaneously to ammonium recovery, where a complex matrix (wastewater) is used. The presence of OMPs was measured in all streams produced in the combined system, allowing to also identify the safety of the recovered ammonia (for example as a fertilizer) or the remain OMPs load in the process line.

2. Materials and methods

2.1. Experimental setup

The OMPs transport was studied in a four compartment electrodialysis (ED) cell (where current is applied), in a two compartment Donnan dialysis (DD) cell (where no current is applied), and over a liquid/liquid membrane contactor (LLMC) using a gas-permeable membrane (additional purification step used after electrochemical ammonia recovery) [29,46]. The four compartments electrochemical cell included a cation and an anion exchange membrane shielding the electrodes, to avoid undesired species reactions such as chlorine gas formation. A simplified scheme is presented in Fig. 1.

The projected surface area of each IEM and each electrode was 100 cm^2. The anode and feed compartment in the ED cell were separated by a CEM Membrane Electrode Assembly (MEA) [46]. Concentrate compartment was separated from feed compartment by a CEM (fumasep FKB-PK-130, Fumatech BWT GmbH, Bietigheim-Bissingen, Germany) and from cathode compartment by an anion-exchange membrane (AEM); fumasep FAB-PK-130 Fumatech BWT GmbH, Bietigheim-Bissingen, Germany). The ED cell was operated at 10 A m^{-2}. The feed and concentrate compartment in the DD cell were separated by a CEM (fumasep FKB-PK-130, Fumatech BWT GmbH, Bietigheim-Bissingen, Germany).

Ammonia was recovered through a gas-permeable membrane (pore size – 200 nm, type – Accurel PP V8/HF, CUT Membrane Technology, GmbH, Germany). The gas-permeable membrane module was supplied with a concentrated sulfuric acid (1 M solution). The ammonia from the concentrate solution was transported over the gas-permeable membrane and recovered in a constant recirculated volume (not refreshed).

All streams were recirculated at constant flow (160 mL min^{-1}). The influent was supplied continuously to the DD cell feed recirculation loop at 0.96 mL min^{-1}. Consequently, the treated feed overflow from the DD cell was supplied continuously and at the same rate to the ED feed recirculation loop. The selected inflow guaranteed that the amount of current supplied to the electrochemical cell was higher than the available TAN charge to be transported across the CEM. The total liquid volumes of the feed (ES cell +DD cell), concentrate, and cathode, including the cell compartments and recirculation vessels were 400 mL each.

2.2. Experimental strategy

A mixture of eighteen OMPs (see Appendix A1, Sigma-Aldrich) was added to synthetic black water (SBW) and digested black water (BW) in a 500 µg L^{-1} concentration. The reasoning behind the OMPs' selection and concentration was 1) to work with a large group of OMPs representing a variety of chemicals for different usage, such as

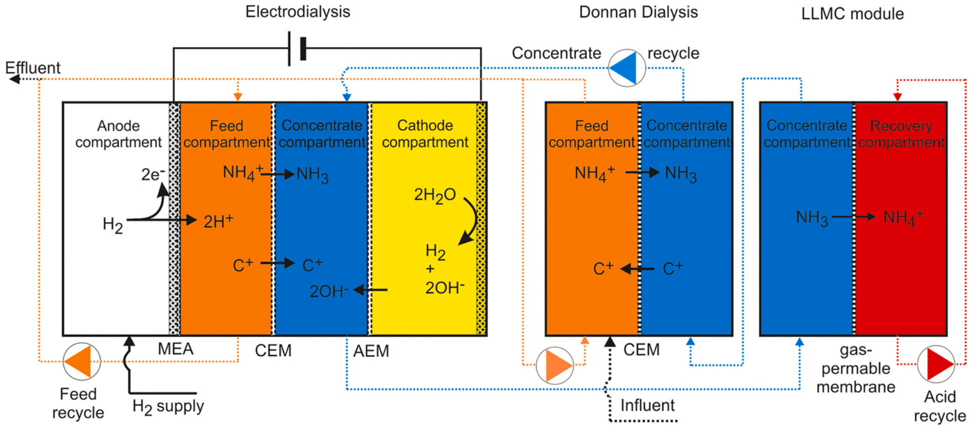

Fig. 1. The organic micropollutant (OMP) transport was characterized over three membranes. The Donnan dialysis (DD) cell contained a cation exchange membrane (CEM), and no current was applied. In DD, species move due to a concentration gradient. In the electrodialysis (ED) cell, the anode reaction generates protons. These protons acidify the supplied influent to the feed compartment and form ammonium (NH_4^+). The applied current drives NH_4^+ over the CEM to the concentrate solution. In the concentrate, NH_4^+ reacts with hydroxide forming ammonia (NH_3). The OH^- ions are produced in the cathode reaction. The NH_3 formed in the concentrate can later be recovered to an acid through a gas-permeable membrane.
Adapted from [46].

pharmaceuticals (e.g., paracetamol), beverages (e.g., caffeine), and herbicides (e.g., diuron), 2) have a concentration within the range found in waste streams [4,10,57,62,66], 3) have a high enough concentration to be detected by the analytical methods used [41]. The selection was based on charge, and therefore 4 positively-, 7 negatively-, and 7 non-charged OMPs were selected. Furthermore, the selected OMPs had a large variability in their physicochemical properties (i.e., charge, hydrophobicity, and size). A complete list of used OMPs with their physicochemical properties is in Appendix A2.

SBW and BW with and without spiked OMPs were supplied to the electrochemical ammonium recovery system for comparison. The BW was the filtered effluent of a lab-scale UASB reactor for phosphate recovery and CH_4 production as described in [14] (10 µm filter cartridge, Van Borselen filters, Netherlands). SBW was composed of the following salts $(NH_4)_2CO_3$ (2.8 g L^{-1}), Na_2CO_3 (0.5 g L^{-1}), K_2SO_4 (0.08 g L^{-1}), KCl (0.5 g L^{-1}) and NaCl (0.3 g L^{-1}) (all purchased from Sigma Aldrich), to approximately match the salt composition of BW without bivalent cations (Ca^{2+} and Mg^{2+}).

After each experiment, the IEMs were replaced with new ones to be able to investigate the behavior of OMPs in the system unimpeded by earlier experiments.

2.3. Chemical analysis

OMP concentrations were analyzed using a liquid chromatography-mass spectrometer (LC-MS Agilent 6420) equipped with a selective electrospray triple quadrupole mass spectrometer for multiple reaction monitoring (MRM) transitions. A Phenomenex phenyl-hexyl column (150 mm × 3 mm, 3 µm pore size) equipped with a guard column was used for chromatographic analysis. The inorganic neutral mobile phase consisted of 2.5 L Milli-Q water, 5 mL Ammonia 5 M, 1 mL Formic acid 99%, and 0.1 mL oxalic acid 1 M. Acetonitrile was used as an organic mobile phase. Before analysis, all samples (1 mL) were spiked with a matrix modifier (50 µL) and an internal standard (50 µL). Agilent Mass Hunter Quant software was used to integrate and quantitate the peaks in the data files.

Samples were collected every hour during the first 10 h after the start and after this period, twice a day over a period four days. Samples were taken from influent, the effluent of the DD pre-treatment, effluent of the ED, concentrate, cathode, and acid. These samples were analyzed for cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (NO_3^-, NO_2^-, Cl^-, SO_4^{2-}, PO_4^{3-}) using a Metrohm Compact IC Flex 930 with a cation column (Metrosep C 4–150/4.0) and a Metrohm Compact IC 761 with an anion column (Metrosep A Supp 5–150/4.0) respectively. The samples were also analyzed for organic carbon, inorganic carbon, non-purgeable organic carbon, and total carbon using a TOC analyzer (TOC-L CPH, Shimadzu Benelux, 's-Hertogenbosch, The Netherlands). Chemical oxygen demand (COD) was determined using a cuvette test kit LCK1414 and a spectrophotometer DR3900 (Hach Nederland, Tiel, The Netherlands).

2.4. Calculations

Removal of OMPs from the supplied influent is given by Eq. (1):

$$OMPs\ Removal_{\mathrm{ED+DD}} = \frac{C_{\mathrm{in}\,f,\ OMP}Q - C_{eff,\ OMP}Q}{C_{\mathrm{in}\,f,\ OMP}Q} \quad (1)$$

Where $C_{\mathrm{inf},OMP}Q$ is the molar flux of a certain OMP in influent [µmol h^{-1}] and $C_{eff,OMP}Q$ is the molar flux of certain OMP in the ED+DD system effluent [µmol h^{-1}].

The removal of OMPs was separated into removal in the DD or in the ED cell by calculating the removal of OMPs over the pretreatment DD (Eq. (2)) and ED (Eq. (3))

$$OMPs\ Removal_{\ DD} = \frac{C_{\mathrm{in}\,f,OMP}Q - C_{DD,OMP}Q}{C_{\mathrm{in}\,f,OMP}Q} \quad (2)$$

Where $C_{\mathrm{inf},OMP}Q$ is the molar flux of certain OMP in influent [µmol h^{-1}] and $C_{DD,OMP}Q$ is the molar flux of certain OMP in DD cell effluent [µmol h^{-1}].

$$OMPs\ Removal_{\ ED} = \frac{C_{DD,OMP}Q - C_{eff,OMP}Q}{C_{DD,OMP}Q} \quad (3)$$

Where $C_{DD,OMP}Q$ is the molar flux of certain OMP in DD cell effluent [µmol h^{-1}] and $C_{eff,OMP}Q$ is the molar flux of certain OMP in the system effluent [µmol h^{-1}].

TAN removal in % is given by Eq. (1):

$$TAN\ Removal\ \ = \frac{C_{\ \mathrm{in}\,f,TAN}\ Q_{\ \mathrm{in}\,f} - C_{eff,TAN}\ Q_{eff}}{C_{\ \mathrm{in}\,f,TAN}\ Q_{\mathrm{in}\,f}} \quad (4)$$

Where $C_{\mathrm{inf},TAN}$ is the TAN concentration in the influent (g_N L^{-1}), Q_{inf} is the inflow supplied to the DD cell (L d^{-1}), $C_{eff,TAN}$is the TAN concentration in the effluent of the ED cell (g_N L^{-1}), Q_{eff} is the effluent flow rate (L d^{-1}).

The ion transport number over the CEM was calculated for all cations (i.e., Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) and is the ratio between the total applied charge (current) and the difference between the ion concentration of the influent and effluent.

$$t_i = \frac{\Delta C_i Q_{\mathrm{inf}} z_i F}{i} \quad (5)$$

Where ΔC_i is the cation concentration difference between influent and effluent (mol L^{-1}), z_i is the net charge of that cation (-), F is the Faraday constant (C mol^{-1}), and i is the current (A).

3. Results and discussion

3.1. OMPs adsorption mechanisms in the CEMs during DD and ED

To understand the behavior of OMPs over CEMs in the DD cell and in the ED cell, the changes in OMPs removal efficiency over time were calculated for each cell (Eqs. (2) and (3)).

Both in DD and ED, two distinct removal regions were observed (Fig. 2). In region I, the removal efficiency decreased rapidly, whereas in region II, steady-state was achieved. Region II demonstrated the system reaches an equilibrium as the same amount of OMPs was removed when the supply was kept constant. The three presented OMPs were a positively charged (lincomycin), a negatively charged (flumequine), and a non-charged (atrazine) OMP. The individual observed behaviors for these three OMPs were representative for other OMPs with the same charge with the exception of Clarithromycin, Dimethoate, and Tetracycline.

The kinetics of each region can be established by adequate data fitting (see Appendix B). During DD an exponential decrease was observed, while during ED has a linear decrease occurred (see Fig. 2, see Appendix B). On the other hand, Region II shows an almost constant removal efficiency over time. During DD the equilibrium removal is close to zero, while for ED the removal efficiency remains around 20% until the end of the experiment. This indicates that when the CEM is conductive, the saturation of the available membrane sites by adsorption is slower. Furthermore, a constant removal efficiency of around 20% in the CEM of the ED cell was surprising. The difference observed between DD and ED can indicate different electrostatic interactions [5,63]. This behavior can be linked to the applied current density (10 A/m^2) [67].

In both DD and ED, negatively charged OMPs showed the lowest removals (initial and equilibrium), see Fig. 3. As previously explained, this was a consequence of the application of CEMs in the system, which are negatively charged membranes.

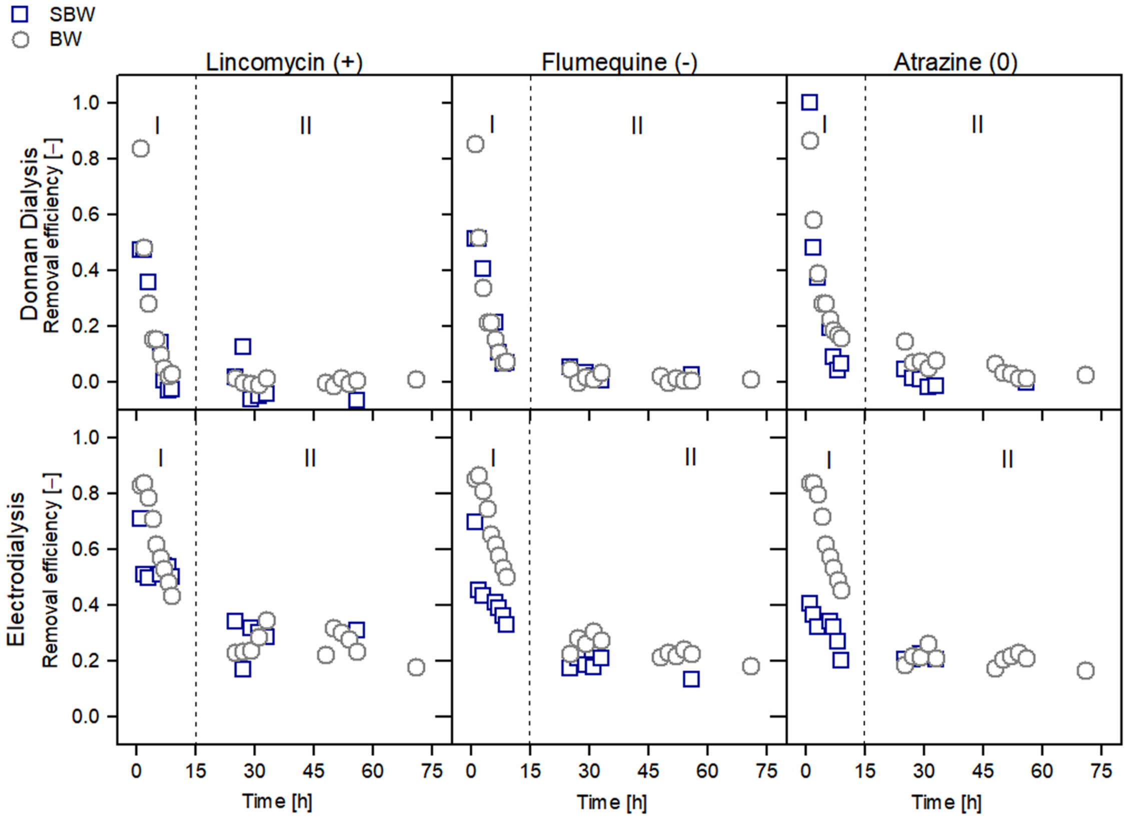

Fig. 2. OMPs removal efficiency over the CEM in the Donnan dialysis cell and over the CEM in the electrodialysis cell in time for three selected OMPs. The OMPs were selected due to their charge i.e., lincomycin (positively charged), flumequine (negatively charged), and atrazine (non-charged). Presented data are from experiments with the application of black water (BW □) and with synthetic black water (SBW ○) as an influent.

Higher removal efficiencies in steady-state (region II) were found in the ED cell compared to the DD cell, see Fig. 3B and D. The presented data confirmed different interaction mechanisms of OMPs in the ED cell and in the DD cell. The ED cell showed more favorable conditions resulting from the applied currents for OMPs adsorption compared to DD. First, in ED, all OMPs were under the influence of an electrical field which accelerated the transport of positively charged OMPs toward the CEMs. Second, because of applied current and electrode reactions in ED, the feed pH decreased and stabilized around pH 5 (Appendix C). To understand the mechanisms of OMPs removal in the DD and in the ED cell, a Pearson's correlation analysis was performed on the removal efficiency for all OMPs physicochemical properties (Appendix A2). In the DD cell, the initial removal efficiency of positively charged OMPs is based on π-π interactions. Because π-π interactions are formed by electrons in overlapping parallel p orbitals between the aromatic ring in OMPs and IEMs [18], a strong linear correlation with the aromatic ring count in BW (Pearson's R = 0.96 with p-value = 0.03) and SBW experiment (Pearson's R = 0.98 with p-value = 0.01) proves their importance in the investigated system. This is also in line with former findings at pH neutral conditions [33,51]. Interestingly, strong and negative correlations were found between the initial adsorption rate and hydrogen donor count in BW (Pearson's R = 0.99 with p-value = 0.03) and between initial adsorption rate and topological polar surface area in SBW (Pearson's R = 0.95 with p-value = 0.03). This opposite correlation is a direct effect of the alkaline feed pH (~9) (Appendix D). Both of these solute properties are a measure of the possibility to form hydrogen bonds, known to be essential in governing the adsorption of positively charged OMPs in CEMs under pH neutral conditions [6,51]. In hydroxide rich conditions, these negatively charged ions can pull hydrogen ions (protons) off the hydrogen donor molecule [68]. This destabilizes the charge of positively charged OMPs and their primary bonding mechanism in CEMs. In the ED cell, where OMPs were under the influence of an external electrical field, and predominantly cation transport takes place, it was found that equilibrium adsorption of positively charged OMPs was based on π-π interactions. This was proven by a strong linear correlation between removal efficiency and aromatic ring count for BW (Pearsons R = 0.97 with p-value = 0.03) and SBW (Pearson's R = 0.97 with p-value = 0.03). Due to more acidic pH in ED than in DD, negatively charged OMPs were adsorbed based on hydrophobic interactions. Adsorption of OMPs at low pH in ED was previously reported [50]. It was shown that acidic conditions accelerate adsorption, as they affect ionization of OMPs e.g., neutralize the charge of negatively charged OMPs. Unlike at neutral pH conditions, at low pH, adsorption is equally high for all OMPs, independently of their charge, by the intensification of hydrophobic interactions [50]. Furthermore, no overall charge changes for all OMPs were observed during the experiments (see Table B2, Appendix B).

Initial removal efficiencies were generally higher in experiments with BW compared to SBW, whereas the equilibrium removal rates were higher in experiments with SBW compared to BW (Fig. 3B and D). This is most likely an effect of the presence of organic matter in the BW. The formation of organic matter-OMPs complexes in the influent could have increased the overall removal of OMPs at the beginning of the process. Previous literature reported a multilayer adsorption between organic matter and OMPs [3,11]. However, after a longer contact time, competition between organic matter and OMPs for the adsorption sites on the membranes could have resulted in lowering the removal efficiencies of OMPs. Blockage of the free volume elements in CEMs, due to the adsorption of hydrophobic fractions of organic matter, prevents the adsorption and thus transport of OMPs without decreasing ion transport. This agrees with other findings described in [1,23]. Looking into the OMPs size, the CEM pores (5–12 nm) should allow the transport of all OMPs [16,53]. However, the shielding effect of organic matter onto CEMs also influenced the CEMs-OMPs interactions in region II

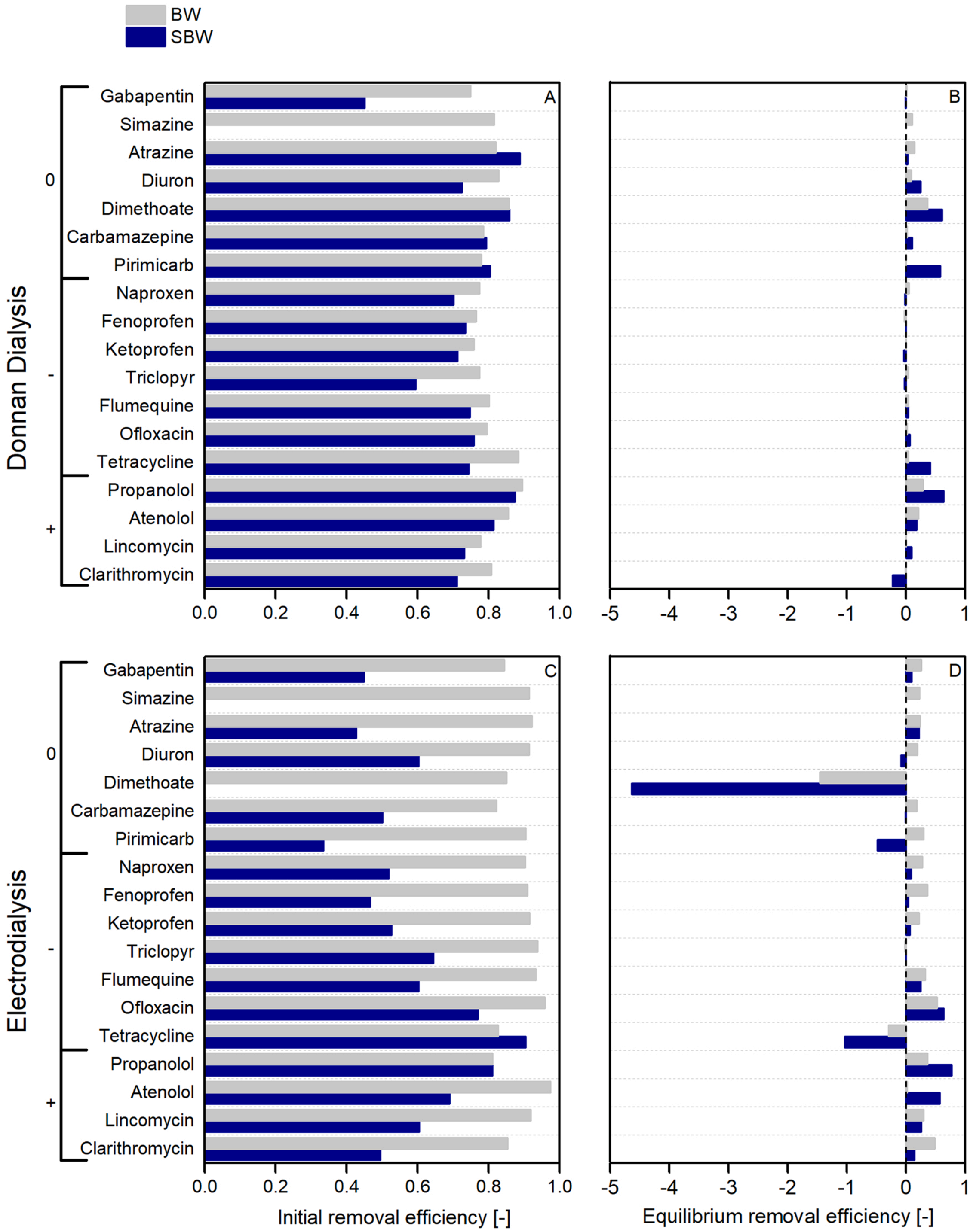

Fig. 3. Initial removal efficiencies (1 h after starting the experiment) of all OMPs in Donnan Dialysis (A) and Electrodialysis (C) cells and equilibrium removal efficiencies (Region II) of all OMPs in Donnan Dialysis (B) and Electrodialysis (D) cells. Presented data are from experiments: with black water (BW) and synthetic black water (SBW) as an influent.

(steady-state). In the experiment with SBW, the effect of high pH was observed by the strong, negative correlation with topological polar surface area (Pearson's R = 0.97 with p-value = 0.05). Due to organic matter-OMPs competition and diffusion of OMPs through the adsorbed organic matter, interactions of OMPs with the membranes were generally weak, and the effect of alkaline pH was negligible. However, it was found that adsorption of OMPs was still governed by the π-π interactions when BW was used as an influent (strong correlation with aromatic ring count; Pearson's R = 0.97 with p-value = 0.02).

Initial adsorption efficiencies of negatively charged OMPs were in both cases (BW and SBW) dependent on hydrogen bonding, as shown by a positive correlation between adsorption rates and hydrogen donor count (Pearson's R = 0.93; p-value = 0.002 and Pearson's R = 0.97; p-value = 0.0002 for BW and SBW, respectively), and topological polar surface area (Pearson's R = 0.96; p-value = 0.0006 and Pearson's R = 0.99; p-value = 0.0004 for BW and SBW respectively) (Appendix A2). Furthermore, the adsorption of negatively charged OMPs is dependent on the size of OMPs: bigger molecules are more easily adsorbed. As described earlier [51], Traube's rule explains the effect of the chain length and molecular size on the adsorption. Specifically, in a situation where the affinity between solute and adsorbent is low, a larger solute size creates a larger contactable surface area between the solute and the adsorbent (membrane), thus a higher likelihood for the OMPs to effectively interact with the membrane. Surprisingly, a strong, negative correlation between the initial adsorption rate and LogD was found, contrary to the previous reports that adsorption of negatively-charged OMPs in IEMs is based on hydrophobic interactions [50,51]. However, previous studies investigated the adsorption of OMPs in the systems where both CEMs and AEMs were used. Here, due to system design, only interactions with CEMs were considered.

3.2. OMP removal and transport through the electrochemical TAN recovery system

Fig. 4 shows the overall removal of OMPs from the supplied influent (Eq. (1)) after 56 h (Fig. 4A) and the total accumulation of OMPs in the concentrate after 56 h (Fig. 4B).

The total load of OMPs was on average 400 μmol of each OMP. Transport of OMPs measured in the concentrate (Fig. 4B) constitutes less than 1% of the total load of OMPs to the system during 56 h. The small amount of OMPs present in the concentrate mainly consisted of positively charged OMPs, i.e., propanolol, atenolol, lincomycin, and clarithromycin (Fig. 4B). This is expected as only negatively charged membranes were in contact with OMPs, meaning only CEMs were used. Nevertheless, the low amount transported can be explained as positively charged OMPs are not easily transported in CEMs systems because of their high affinity toward CEMs. Adsorption of positively charged OMPs limits their diffusion, even when high concentration differences are developed, and the steady-state is achieved over the compartments [33]. The limiting effect of adsorption onto diffusion of positively charged OMPs is related to blocking of the transport channels by adsorbed OMPs. If 40% was still being removed (see Fig. 4A), and only 1% was transported (see Fig. 4B), the OMPs were adorbed. Additionally, the low pH of the feed solution limits the transport of OMPs by enhancing their adsorption onto membranes, as reported previously [1,50].

Combining the results from Fig. 4A and B, the OMP removal from the influent should be associated with OMPs accumulation in the system. Most likely, the OMPs adsorbed to the CEMs [51]. This is supported by the high removal (up to 80%) of positively charged OMPs (propanolol, atenolol, lincomycin, and clarithromycin) and the inability to detected these OMPs in the concentrate solution. The system creates privileged conditions for the adsorption of all OMPs (positively, negatively, and non-charged) due to low pH conditions on the feed side, which affects the ionization of negatively charged OMPs. Furthermore, in the moderate or high surface density regions, the adsorption considerably increases at higher voltages. Briefly, the adsorption occurs at regions of complementary charge, leading to more oriented and efficiently packed/adsorbed molecules at higher voltages. This enhances the adsorption of positively charged OMPs. Also, Fig. 4B shows a higher transport of OMPs when SBW was supplied as an influent compared to BW. This difference can also be the result of the presence of organic matter. Organic matter adsorbing onto membranes can shield the membrane surface and thus serve as an "additional barrier" against OMP transport [5].

Fig. 4A shows that some OMPs had a negative removal efficiency, i.e., dimethoate (for both BW and SBW), clarithromycin (for SBW), or tetracycline and atenolol (for BW). The negative removal efficiency value is related to desorption. Desorption from CEMs is a time-dependent phenomenon as its effect decreases with time (see Appendix C). However, in this study cases of negative removal seem random (except for dimethoate), and there is no significant correlation between desorption and any of the parameters of OMPs. Unfortunately, due to the complicity and design of the experiment the membranes could not be analyzed in detail to draw further conclusions about the interactions between OMPs, organic matter and the membranes. Further studies, should be designed to allow the separated measurement of the influence of pH, charge, hydrophobicity, and the presence of organic matter.

3.3. Overall transport of OMPs vs. ionic species

During TAN recovery, the OMPs and other components in BW are exposed to different applied forces (concentration gradients, applied electric field) and environment changes (pH, conductivity). Although OMPs can be categorized based on their charge, they do not necessarily behave like other charged species. Although we observed that positively charged OMPs were removed from the influent and transported through the CEM more than negatively charged and uncharged OMPs, the removal of all OMPs was also dependent on adsorption to the CEMs and interaction with organic matter. Cation transport over the CEM in the ED cell was constant through all experiments; ammonium was the

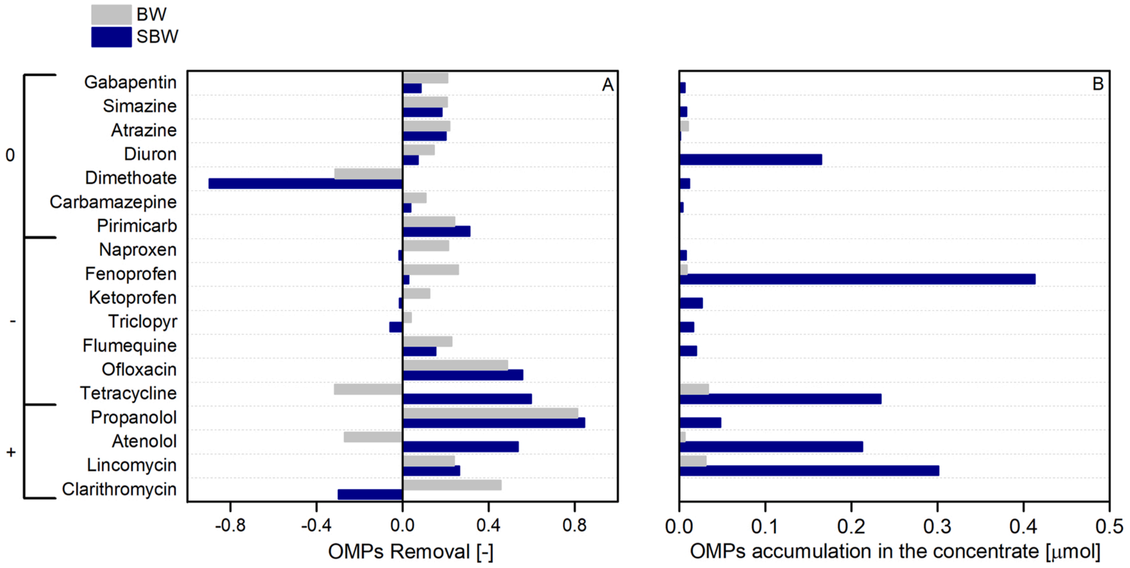

Fig. 4. The overall removal efficiency of OMPs over the CEMs from the supplied influent (Fig. 4 A) and the total accumulation of OMPs measured in the concentrate (Fig. 4B). The total accumulation was less than 1% of the total load of OMPs to the system. Two experiments were performed: with black water (BW) and with synthetic black water (SBW) used as an influent. Presented data was measured after 56 h of experimentation, where transport and removal achieved a steady-state while continuously supplying wastewater.

predominantly transported ion (around 60%) described in [46]. The remaining charge is mostly transported by other competing cations. Finally, we observed lower mobilities of OMPs in CEMs compared to NH_4^+, Na^+, and K^+ as previously reported [4,33,41].

The electrochemical ammonia recovery system removed 85.5% ± 2.8 of the TAN from the BW while operating at 10 A m^{-2}. When supplied with SBW, the TAN removal was 96.0% ± 1.3. The ammonium removal and transport was comparable to previous studies [13,27,49,60]. The excess of OMPs in the spiked solution did not affect the ion removal of the system.

3.4. No OMP transport through the gas-permeable membrane

For further purification, electrochemical systems for ammonium recovery are often combined with gas-permeable membranes [13,47,49]. Ideally, these membranes should only allow the passage of volatile substances. Nevertheless, their pore size is around 200 nm and water transport was previously reported [38,44]. Therefore, we also characterize the passage of OMPs from the concentrate solution to the recovered product.

No OMPs were detected in the samples taken from the acid compartment, where the ammonium product is formed ($(NH_4)_2SO_4$). When using two types of membranes such as cation exchange and gas-permeable membrane: 1. for neutral and negative OMPs, there is a double barrier against transport (CEM in ED & DD and gas-permeable membrane); 2. for positively charged OMPs, the transport to the concentrate occurs, but the gas-permeable hydrophobic membrane prevents their transport to the product (acid) compartment.

Thus, we concluded that OMP transport toward concentrate did not pose a risk for the possible ammonium products recovered by electrochemical systems. Therefore, the product could be used as a nitrogen source for crop growth or protein production [42,45,62].

4. Conclusions

In this work, we studied the fate of organic micropollutants during electrochemical ammonia recovery using synthetic and real black water from a lab-scale UASB reactor designed for methane production and calcium phosphate recovery. Adsorptions of organic micropollutants to the cation exchange membrane was the main removal mechanisms. The cation exchange membrane in the electrodialysis cell showed a higher equilibrium removal than the cation exchange membrane in the Donnan dialysis cell. This occurred as the electrodialysis cell had more favorable conditions for organic micropollutants adsorption compared to Donnan dialysis. Only small amounts of positively charged organic micropollutants accumulate in the concentrate (~1%). The product recovered (ammonia concentrate) through the gas-permeable membrane was free organic micropollutants.

CRediT authorship contribution statement

Mariana Rodrigues: Methodology, Investigation, Writing – original draft, Visualization. **Malgorzata Roman:** Methodology, Investigation, Writing – original draft, Visualization. **Annemiek ter Heijne:** Writing – review & editing, Supervision. **Tom Sleutels:** Writing – review & editing, Conceptualization. **Emile R. Cornelissen:** Writing – review & editing, Supervision. **Arne Verliefde:** Writing – review & editing, Supervision. **Cees J.N. Buisman:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Philipp Kuntke:** Resources, Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

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

Data availability

The research data underlying this work is available at https://doi.org/10.4121/14744040.v1.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.109613.

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