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ABSTRACT

Electrodialysis (ED) is a promising emerging electrochemical membrane technology for nutrient concentration and recovery from wastewater. However associated environmental safety aspects have to be assessed before utilizing concentrated nutrient produced by ED, for instance as fertilizer. Municipal wastewaters contain various micropollutants that have the potential of being concentrated during the ED treatment processes. This study quantified the transport of pharmaceuticals during ED nutrient recovery from synthetic centrate wastewater. Specifically, it is evaluated whether pharmaceutical micropollutants are mobile, and therefore able to transport across the cation exchange membranes and concentrate into the ED concentrate product. Results demonstrate that NH_4^+-N, PO_4^{3-}-P and K^+ could be concentrated up to 5 times in the concentrated ED product (3700–4000 mg/L NH_4^+-N, 21–25 mg/L PO_4^{3-}-P, 990–1040 mg/L K^+). Target micropollutants, such as diclofenac, carbamazepine and furosemide were largely retained in the diluent, with less than 8% being transported across to the concentrate product (feed micropollutant concentration 10 or 100 µg/L) based on the final target pharmaceutical amounts in the ED concentrate product (µg). Some transport of micropollutants such as atenolol, metoprolol and hydrochlorothiazide was observed to the concentrate product. For instance a final concentration of

10.3, 9.4 and 8.6 µg/L on average was measured for these pollutants in the final ED concentrate product (final volume ~1 L) in experiments with a feed water (initial volume 20 L) containing only 10 µg/L of target pharmaceuticals. Transport of pharmaceuticals across the ED membranes was concluded to be dominated mainly by the molecule hydrophobicity/hydrophilicity as well as electrostatic interactions between pharmaceutical molecules and ED membranes. Particularly excluded were those having a negative charge and high hydrophobicity such as diclofenac and ibuprofen.

Keywords:

Electrodialysis

Membrane

Micropollutants

Nutrient recovery

Municipal wastewater

1 Introduction

Fertilizer prices are increasing globally due to increased demand, increased energy costs, and resource limitations such as depleting phosphorus reserves (Batstone et al. 2015, FAO 2017, Mehta et al. 2015). This has increased focus on enhanced nutrient recovery. A substantial fraction of macronutrients such as phosphorus, potassium and nitrogen (100% P and K, 50% N) could be recovered from existing waste streams such as agricultural and municipal wastewater effluents (Batstone et al. 2015, Mehta et al. 2016). Electrodialysis (ED) is an emerging electrochemical membrane process, where anions and cations are migrating through cation exchange membranes (CEMs) and anion exchange membranes (AEMs) due to electrical current, which is generated by applying potential to the terminal electrodes (Baker 2004).

Zhang et al. (2009) studied the utilization of ED for the separation of nutrient ions and organic compounds from salts in synthetic reverse osmosis (RO) concentrate. Nitrate (NO_3^-) and phosphate ions ($H_2PO_4^-$ and HPO_4^{2-}) could be readily removed from the synthetic RO concentrate, removal rates of 92% for NO_3^- and 86% for the phosphate ions was achieved, separation of monovalent ions such as NO_3^- could be further enhanced to 98% by using monovalent selective membrane. Although the separation of nutrients from the organic fraction of the RO concentrate was possible, the separation of salts from nutrient ions was difficult as salts were transported together with the nutrient ions. ED was used by Wang et al. (2015) for the simultaneous recovery of ammonium and phosphorus from synthetic wastewater simulating side streams of anaerobic digestion by coupling ED with a struvite reactor. Removal ratios of 96–100% for ammonia salt and 86–94% for phosphate could be reached by integrated process of ED and struvite crystallization. Zhang et al. (2013) used similar approach to separate and recover phosphate from industrial anaerobic effluent of potato processing wastewater. Zhang et al. (2013) reached over 7 times increase in the concentrate phosphate concentration (from 0.93 to 6.64 mmol/L).

Ward et al. (2018) demonstrated pilot scale nutrient recovery performance utilizing an ED process containing a 30-cell pair ED. This pilot study utilized domestic anaerobic digester supernatant, which had been passed through a centrifuge and a struvite crystallization process, as a feed source (centrate). A concentrated product (NH_4-N 7100± 300 mg/L and K 2490± 40 mg/L) could be achieved by concentrating nutrient ions from the centrate wastewater dilute feed stream to the concentrate product stream using the ED process. The electrode power consumption was 4.9 ± 1.5 kWh/kgN, averaged across the three replicate trials. This value is lower than competing technologies for NH_4-N removal and production, and far lower than previous ED lab trials, and demonstrates practical economic and commercial viability of the technology.

Although ED have proven to be a promising technology for the resource recovery from wastewaters, it is also important that the valuable resources recovered with ED do not cause any risks for the environment. The various waste streams of municipal wastewater treatment may contain significant amounts of micropollutants, which may hinder the utilization of fertilizer products obtained by emerging technologies such as ED. According to Falas et al. (2016), many micropollutants are biologically recalcitrant to wastewater treatment processes and thus are not readily degraded during treatment. According to Gao et al. (2016), Zhu et al. (2014) and Arola et al. (2017) the concentrations of micropollutants such as carbamazepine, caffeine and diclofenac can vary significantly depending on the waste streams, concentration ranges from 0.05–5 µg/L up to 0.1–100 µg /L being reported in the waste streams of municipal wastewater treatment. Thus, it is important to identify whether micropollutants can migrate through the ED membranes or accumulate in the concentrate product.

Limited studies have been conducted related to the removal of pharmaceuticals utilizing ED in wastewater treatment applications (Banasiak et al. 2011, Pronk et al. 2006, Vanoppen et al. 2015). Pronk et al. (2006) evaluated ethinylestradiol, diclofenac, carbamazepine, propranolol and ibuprofen from urine by continuous laboratory scale ED. These were preferentially retained in the feed stream (>95% retained by ED membranes) and hence excluded from concentrate product. For analytical reasons the target micropollutants were spiked in the urine at concentrations up to 10µM (>2 mg/L), at levels well above normal sewage. Ethinylestradiol was completely retained by ED membranes over the whole experimental period of 90 days. Retentions for other pollutants were very high initially (≥95% for first 10–20 days), but some breakthrough especially for propranolol and ibuprofen occurred during extended operation (90 days). The main retention mechanisms for

these micropollutants were identified to be membrane adsorption/partitioning and diffusion (Pronk et al. 2006).

Banasiak et al. (2011) studied the sorption of pesticide endosulfan and the hormone estrone by ED membranes. Sorption was studied by treating a background solution (5 g/L NaCl and 84 mg/L of $NaHCO_3$), containing 2.5 mg/L of each pollutant, in a continuous laboratory scale ED (dilute feed and concentrate recirculated to one feed reservoir). 67% of the endosulfan and 42% estrone (596 and 381 $\mu g/cm^3$) was adsorbed to the ED membranes during 14 h ED experiments with a neutral feed solution (pH 7). At an increased pH of 11, the sorption decreased to 47 and 31% for endosulfan and estrone potentially due to competitive sorption between degraded/dissociated endosulfan and estrone and the ion-exchange membranes. Whilst a significant amount of pesticide endosulfan and estrone hormone could be rejected from the concentrate product with ED, an accidental release of these adsorbed pollutants from the membranes for instance during membrane cleaning would result in environmental aquatic discharge (Banasiak et al. 2011).

Vanoppen et al. 2015 studied the transport of trace organic contaminants such as carbamazepine, diclofenac, ketoprofen and metoprolol through ED membranes in saline water matrix (10 or 100 g/L NaCl). It was concluded that the transport of organic contaminants like carbamazepine, diclofenac and metoprolol (<20% transport through ED membranes in most cases) was mainly result of electrostatic interactions and overall the transport was mainly driven by diffusion. For uncharged contaminants the diffusion driven by concentration difference, together with the affinity for the membrane were the main drivers for the transport of the target contaminants whereas the molecule size was less significant.

Due to very limited studies on the fate of micropollutants in the ED processes, especially with feed solutions containing ambient concentrations of pollutants, and with domestic wastewater (rather than urine), this study aims to better evaluate the fate of micropollutants through the ED process. Thus, this study aims to examine if pharmaceuticals can migrate across the ion exchange membranes to the concentrated product during short-term ED experiments (8 h) with synthetic wastewater and to identify the determining factors for possible transfer of pharmaceuticals. If the transport of pharmaceuticals to the concentrate product can be minimized or prevented completely, the utilization of the concentrate product for fertilizer applications becomes more feasible.

2 Materials and Methods

2.1 ED unit configuration and operating procedure

Experiments were performed in a batch-mode with a laboratory scale ED unit supplied by ABR Process Engineering (Brisbane, Australia), with electrolyte rinse solution (initial volume 10.0 L), product (hereafter named as concentrate product, initial volume 0.6–0.65L) and dilute feed (initial volume 19.6–19.65 L) being recirculated through reservoirs. The ED unit was equipped with five CEMs (General Electric CR67) and four AEMs (General Electric AR204SZRA), each with an effective area of 10 X 15 cm (150 cm^2), and a 4 mm spacing. The ED membranes had the following characteristics (CEM and AEM): membrane thickness 0.6 mm and 0.5 mm, ion exchange capacity 2.1 and 2.4 meq/g, pH stability 0.5–12 and 0.5–10.5 and resistance (0.01N NaCl) of 10 and 7 Ω/cm^2 (data from the manufacturer). The anode and cathode were Ir MMO mesh coated with titanium (ABR Process Development, Brisbane, Australia). The configuration of the ED unit consisted of 4.5 cell pairs, an anode chamber, a cathode chamber, four product chambers and four dilute feed chambers (Fig. 1). An additional cation exchange

membrane was fitted to the cathode chamber to prevent the migration of chloride ions into the electrolyte rinse solution.

[Figure 1 to be put here from a separate Figures document]

Fig. 1 Schematic diagram of the used ED setup.

The dilute feed, electrolyte rinse solution and concentrate product reservoirs were ventilated to maintain atmospheric pressure. A potentiostat (Manson model HC3104) was used to supply a constant current of 0.5 A (33.3 A/m^2). The 0.5 A current used was in a similar ranges utilized by Thompson Brewster et al. (2017), Wang et al. (2015), Zhang et al. (2009) and Zhang et al. (2013) in laboratory scale ED experiments. The concentrate product and dilute feed stream had a constant flow rate of 23 mL/min each and they were recirculated back to their respective reservoirs during ED experiments. Sulfuric acid (H_2SO_4, 1.5 mL/L) was used as electrolyte rinse solution and was supplied to the anodic and cathodic compartments at the same flowrate of 23 mL/min and was recirculated back to the electrolyte rinse solution reservoir during ED experiments. The conductivity of the electrolyte rinse solution was maintained by between 10 and 15 mS/cm during ED experiments by dosing 0.3–0.5 mL/L H_2SO_4 to the reservoir when conductivity decreased below 10 mS/cm.

Synthetic wastewater (pH 8.5) having a similar composition of NH_4^+, Na^+ and K^+ as post-crystallized centrate (supernatant from the centrifugation of anaerobic digestate after struvite crystallization) was used in ED experiments as a dilute feed (Table 1, Thompson Brewster et al. 2017 and Ward et al. 2018). Duration of each experiment was 8 h and 10 ug/L (treatment 1) and 100 ug/L (treatment 2) micropollutant dilute feed concentrations were tested to determine the effect of micropollutant concentration in the dilute feed to the micropollutant transport across the membrane. Triplicate 8 h experiments were conducted, and a stronger initial concentrate product solution treatment was also tested (5510 mg/L NH_4^+, 6317 mg/L Na^+, 1513 mg/L K^+, 44.4 mg/L

160 Ca^{2+}, 26.5 mg/L PO_4^{3-}P, treatment 3). This was done to study the effect of osmotic water transport
161 on the migration of target pollutants across the ED membranes. As the product concentration
162 overall increases the osmotic transport of water will change, which may influence the transport of
163 target compounds, and relative proportioning for migration may change. The ED cell was cleaned
164 with 0.5% HCl solution (3 h cleaning) after each experiment. Samples (dilute feed, feed out,
165 electrolyte rinse solution and concentrate product) were taken at the beginning and at the end of
166 each experiment. Sample volumes were 1.5 mL for the micropollutant analyses (taken directly to
167 glass HPLC vials) and 50 mL for other analyses (taken to 50mL plastic sample containers). 1.5
168 mL micropollutant samples were kept in the freezer before analysis and 50 mL samples were kept
169 at 4°C after sampling before analysis.

170 Table 1 Average properties of synthetic wastewater used as dilute feed stream in ED experiments.

171 [Table 1 to be put here from a separate Tables document]

172 **2.2 Desorption study**

173 The potential adsorption of micropollutants to the ED membranes was studied in a separate 24h
174 desorption experiment, where methanol-water (50/50) desorption solution containing 45 g/L NaCl
175 was used to desorb the pharmaceuticals from the ED membranes after extended 24 h ED
176 experiment with a target pharmaceutical concentration of 100 µg/L. Methanol and NaCl have been
177 utilized for the desorption purposes before to desorb micropollutants such as diclofenac from
178 adsorption membrane and ion exchange resins (He et al. 2017, Laundry and Boyer 2013).
179 According to Laundry and Boyer (2013) the combination of methanol and NaCl provides efficient
180 desorption ability especially for diclofenac, since the NaCl provides counter ions for the ion
181 exchange as a form of Cl^- ions and the interactions with a less polar solvent methanol enables the
182 desorption. For diclofenac both are required to reverse the sorption process (Laundry and Boyer
183 2013). Thus, combined solution of methanol and NaCl was chosen as desorption solution. The ED

cell was rinsed after the experiment with Milli-Q water for 30 min before desorption experiments. The desorption solution was then recirculated through the ED cell for 24 hours after the rinsing and solution was sampled at 2- and 24-hour period of desorption.

2.3 Target micropollutants

Target micropollutants were chosen based on the widespread presence in the effluents of anaerobic and aerobic municipal wastewater treatment (Gao et al. 2016, Zhu et al. 2014, Arola et al. 2017). Micropollutants used comprised of atenolol, caffeine, carbamazepine, diclofenac, furosemide, hydrochlorothiazide, ibuprofen, metoprolol and trimethoprim (Table 2). Most of these nine pollutants are unreadily removed in traditional municipal wastewater treatment processes (Falas et al. 2016, Arola et al. 2017). Samples for the micropollutant analyses were taken directly from the dilute feed, electrolyte rinse solution and concentrate product reservoirs and post ED dilute samples were taken directly from the post ED dilute line, since the post ED dilute stream was also recirculating back to the dilute feed reservoir.

Table 2 presents also the acid dissociation constants pKa, which describe the acidity of a specific molecule. If pKa value of a pollutant is lower than the pH of wastewater it is considered to be dissociated and negatively charged (Sui et al. 2010, Thomas and Foster 2005). Log K_{ow} describes the hydrophobicity/hydrophilicity of a substance. If log K_{ow} value is higher than 3.2 the substance is considered to be clearly hydrophobic and might have higher tendency to adsorb into membrane structure if hydrophobic (Tadkaew et al. 2011, Sui et al. 2010, Hai et al. 2011).

Table 2 Molecular characteristics of the studied micropollutants and their concentrations in the ED dilute feed stream (pH 8.5).

[Table 2 to be put here from a separate Tables document]

2.4 Analytical techniques

Elemental analysis was performed from the 50 mL samples by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 7300DV, Waltham, MA, USA) for total cation concentrations (calcium, sodium, potassium, magnesium). Lachat QuickChem8500 Flow Injection Analysis (FIA) (Lachat Instruments, Loveland, CO, USA) was used to measure NH_4^+-N, PO_4^{3-}-P, NO_x-N and NO_2^--N. During each experiment the pH and conductivity of all solutions was measured with TDS Aqua-CPA (ISO 9001:2008) pH and conductivity meter (k=10 sensor). Total solution volumes were also measured at the start and end of the experimental period (dilute feed, concentrate product and electrolyte rinse solution volumes in the reservoirs).

Target micropollutants studied in this work were analyzed by ultra-fast liquid chromatography (UFLC) coupled with mass spectrometry (MS). A volume of 20µL of sample was injected in a Shimadzu UFLC connected to an AB Sciex 4000QTrap QLIT-MS equipped with a Turbo Spray source. The UFLC instrument was equipped with a 5µm, 250×4.6 mm Altima C18 column (Grace), which was operated at 40°C. Each sample was analyzed separately in both positive and negative ion multiple reaction monitoring (MRM) mode. In positive mode the eluent A was 95% acetonitrile / 5% HPLC grade water (v/v) and eluent B was 1% acetonitrile / 99% HPLC grade water (v/v); both containing 0.1% formic acid. The flow rate was 1 mL/min and the elution gradient started with 15% of eluent A, increasing to 100 % in 12.5 minutes and held isocratically for 2.5 minutes. The eluent returned then to initial conditions in 0.2 minutes and the column was re-equilibrated for 6 minutes leading to a total time of 21.2 minutes. In negative mode the eluent A was 50% acetonitrile / 50% methanol (v/v) and eluent B was HPLC grade water. The flow rate was 1 mL/min and the elution gradient started with 15% of eluent A, increasing to 90 %

in 7 minutes and held isocratically for 3 minutes before rising to 100% in 2 minutes and held isocratically for 5 minutes. Then the eluent returned to initial conditions in 2 minutes and the column was re-equilibrated for 5 minutes leading to a total time of 24 minutes. Two transitions were monitored in the MRM mode. The first transition was used for quantification and the second one for confirmation purposes only. The quantification was performed using 8 points external calibration curves obtained from the injection of standard solutions ranging from 0.1 to 100 µg/L. Linear or quadratic regression was used depending on the compound, which gave good fits with R2 values above 0.99.

2.5 Molar ionic flux and current efficiency

The molar ionic flux (J_i) across the cation exchange membranes was determined for NH_4^+-N, Na^+, K^+ and Ca^{2+} at 1 and 8 hours of ED operation from a mass balance by using equation 1.

$$Ji = \frac{Q2*C2-Q1*C1}{A} \quad (1)$$

,where C1 is the concentration (mol/L) of respective cation in the post ED dilute stream (flow out from the ED cell) and C2 is the concentration (mol/L) of respective cation in the dilute feed (feed into the ED cell), Q_1 is the flow rate out of the ED cell (L/h), Q_2 is the flow rate to the ED cell (L/h) and A is the total cation exchange membrane area (m^2).

Current efficiency (CE) is defined as the ratio of moles transferred of the target cation with time compared to the faradays of electricity passed through the ED cell. Equation 2 was used to determine the theoretical molar transport capacity.

$$TC(theoretical) = \frac{NtI}{FV} \quad (2)$$

where TC (theoretical) is the theoretical transport capacity, N is the number of cell pairs stacked in the ED cell, t is the duration of the experiment (s), I is the average current density (A/m^2), F is the Faraday constant (96486 C/mol) and V is the volume of the cell (L).

The measured transport is determined using equation 3.

$$TC\ (measured) = \sum n_i z_i \quad (3)$$

where the TC (measured) is the measured transport from the experiment, n_i is the moles of species i per L and z_i is the valency of the species i. The overall CE is the measured transport capacity over the theoretical transport capacity. The species i consisted of the major cations K^+, Na^+, Ca^{2+} and NH_4^+-N.

2.6 Analysis of Variance (ANOVA) on ionic flux

Analysis of variance (ANOVA) was done to determine if flux was impacted by treatment (10 µg/L, 100 µg/L, 100 µg/L strong product), categorical factor with three levels – treatment 1, 2, 3, or time (1h vs 8 h), also effectively categorical. ANOVA was done using the anovan command in Matlab R2018b. Interactions were checked, but were never significant, and not used for the main model. A 5% significance threshold was applied, and p-values reported for significant effects.

3 Results and Discussion

3.1 Ionic flux, efficiency and concentration of nutrient ions

The ionic flux of the major cations that migrated from the dilute feed to the concentrate product compartments was estimated by equation 1. Highest overall ionic fluxes (J_i, $mol.m^2h$) for the major cations, being 0.43 ± 0.06, 0.31 ± 0.07, 0.05 ± 0.007 and 0.001 ± 0.0002 mol/m^2h for NH_4^+-N, Na^+, K^+ and Ca^{2+}, and 0.001 ± 0.0001 mol/m^2h for PO_4^{3-}-P were obtained in the ED treatment 1 (10 µg/L pollutant concentration). Figure 2 shows the average ionic fluxes (J_i, mol/m^2h) for the 1 and 8-hour operating periods in all ED experiments with a dilute feed

micropollutant concentrations of 10 and 100 µg/L (treatment 1 and 2) as well as in the experiments with strong initial product (treatment 3). Small decrease in the ionic fluxes (0–19%) was observed overall over the experimental period for all major ions, mainly in treatment 1 and 2. ANOVA indicated that treatment was always a significant factor (mainly with treatment 3) with p-values of $0.02\text{-}1\times10^{-5}$ (Table SI1). Time was significant (causing a decrease in ionic flux) for K^+ (p=0.001) and NH_4^+ (p=0.01). The largest decrease in the average ionic molar flux (mol/m^{2}h) was 19% for the anion PO_4^{3-}-P in the ED treatment 1 (t-test p=0.025). This decrease can be expected as the product EC becomes higher the transfer of ions decreases by back-diffusion. Precipitation as calcium phosphates is unlikely, as Ca^{2+} and PO_4^{3-} was very small in the feed (4.6-4.8 mg/L, Table 1), and calculated solublity indices were generally an order of magnitude lower than for published precipitation indices ($CaHPO_4$, $Ca_3(PO_4)_2.xH_2O$ (Musvoto et al., 2000). More likely the partial depletion of phosphate in the feed water during the ED treatment (17.5, 19.1 and 14.2% depletion of PO_4^{3-}P on average in the treatment 1–3) decreases the phosphate flux.

[Figure 2 to be put here from a separate Figures document]

Fig. 2 Average ionic fluxes (J_i, mol/m^{2}h) for the 1 and 8-hour operating periods in the triplicate ED experiments with a dilute feed micropollutant concentrations of 10 (treatment 1) and 100 µg/L (treatment 2) as well as in the experiments with strong initial product (treatment 3). ED operated 8h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min. (n=3, error bars = 95% confidence interval).

The total current efficiency for the transfer of all cations (K^+, Na^+, Ca^{2+} and NH_4^+-N) across the CEM membranes was calculated by the equation 2 and 3. The average total current efficiency for the experimental period was 66 ± 1% (NH_4^+-N transport 57%, K^+ transport 6%) in the treatment 1 (10 µg/L pollutant concentration), 63 ± 2% (NH_4^+-N transport 58%, K^+ transport 6%) in the treatment 2 (100 µg/L pollutant concentration) and 57.8 ± 0.2% (NH_4^+-N transport 58%, K^+

297 transport 6%) in the treatment 3 (100 µg/L pollutant concentration, strong initial product). The
298 initial total current efficiencies were between 57.9 and 66.7 % on average and decreased to 57.6-
299 64.8% over the 8-hour experimental duration. These values were lower than reported by Ward et
300 al. (2018) for pilot scale ED, who reported average total current efficiency of 76 ± 2% (NH_4-N
301 transport 40%, K transport 14%) for all major cations over the experimental period. A
302 concentration factor of 5 ± 0.5 was achieved in the ED experiments with the dilute feed (treatment
303 1 and 2) for the nutrient ions NH_4^+-N, PO_4^{3-}-P, K^+ and Ca^{2+} (Table 3). For instance for the NH_4^+-
304 N the initial concentration was around 750–770 mg/L in the initial feed (treatment 1 and 2, feed
305 volume 19.6–19.65 L) and around 3700–4000 mg/L in the final concentrate product (final product
306 volume 1.0–1.1 L, initial product volume 0.60–0.65L, 2% transport extent). Thus, around 26 % of
307 the ammonia present in the initial feed was removed and the feed conductivity decreased from the
308 initial 10.3–10.5 mS/cm to the 7.8–8.7 mS/cm by the end of the experiments (average conductivity
309 removal around 21%).

310 A reduction in the ionic molar flux at high product concentrations has been previously
311 reported (Ward et al. 2018). Rottiers et al. (2014) identified back diffusion of ions from the
312 concentrate to dilute stream due to a concentration gradient as a major limiting factor for ion
313 concentration and efficiency in ED processes, and the type of membranes only marginally
314 influenced this. Thompson Brewster et al. (2017b) suggested that limitations to high product
315 concentrations might be due to increased back diffusion due to large concentration gradients, and
316 osmotic and electro-osmotic water fluxes. Mondor et al. (2008) reported the NH_4^+-N concentration
317 was partly limited by osmosis and the transfer of solvated ions from the dilute feed stream to the
318 concentrate product stream, and as the concentrate ionic strength increases, solvated ion water
319 transport limits the concentration extent. This finding was also supported by Ward et al. (2018).

Table 3 Average concentrations of NH_4^+-N, PO_4^{3-}-P, K^+ and Ca^{2+} in the ED dilute feed and final concentrate products as well as their concentration factors during ED experiments. ED operated 8h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min. (n=3).

[Table 3 to be put here from a separate Tables document]

A NH_4^+-N ion concentration factor of 5 achieved in this study was quite low when compared to the 8.77 reported by Ward et al. (2018) in the pilot scale electrodialysis. Although Ward et al. (2018) utilized the same membranes used in this experimental work, the volume ratios utilized by Ward et al. (2018) were different, which explained the difference. Results obtained by Ward et al. (2018) for the current density vs voltage when operated in the range of 0.8 and 4 mA/cm^2 showed a linear increment in voltage, as the current density increased from 0.8 to 3.2 mA/cm^2, the ohmic region was identified. A sharp decline in slope was then observed suggesting increased resistance due to concentration polarization or depletion of ions in the boundary layer of membrane. Based on the slopes of the ohmic and the plateau regions, the 33A/m^2 used in this work was 60% higher than Ward et al. (2018) and would have fallen into the concentration polarization area of the plot, therefore the water splitting region or the over limiting current density was reached (Strathmann, 2010). Due to this the obtained average ionic flux were high when compared to ones reported by Ward et al. (2018) in the treatment of centrate wastewater with a pilot scale ED. High ionic fluxes were also expected, since the ED experiments were conducted at laboratory scale with a simple water matrix, which did not contain impurities able to foul the membranes, like in real wastewaters. Organic impurities present in the real wastewaters can also interact with cations via ion-pairing, activity changes, and other interactions (Stumm and Morgan, 1996), which will have an effect to the ionic fluxes. The operation of the ED cell in the limiting current density area would have also resulted in lower current efficiencies (58–66% in this study compared to 76% reported by Ward et al. (2018)) due to current being used to split water on the membranes.

3.2 Transport of pharmaceuticals during ED

Transport of target micropollutants, all being pharmaceuticals, through the ion exchange membranes to the final ED concentrate product during ED experiments are illustrated in the Figures 3 and 4. Ion exchange membranes excluded (<0.6% pollutant transport, Table 4) diclofenac, ibuprofen, furosemide as well as carbamazepine and caffeine efficiently from the concentrate product in the ED treatment 1, total amount of these pollutants being below 1.2 µg (corresponding to concentrations <1.22 µg/L) in the final concentrate product with a nutrient concentration factor of 5 (Fig. 3). Similar trend was observed in the ED treatment 2 and 3 (Fig. 4). However, the transport of other pollutants atenolol, metoprolol, hydrochlorothiazide and trimethoprim to the final concentrate product was more intense during ED experiments (0.4–7.4% pollutant transport, Table 4). The results indicates that atenolol and metoprolol are either accumulating to the final concentrate product (pollutant concentration µg/L higher in product than in the initial feed) or proportioning (pollutant splits between product and diluent compartments according to hydraulic changes including osmotic transfer to concentrate) whereas trimethoprim and hydrochlorothiazide are proportioning and other pollutants are retained (rejected by the membranes in comparison with water). The concentrations of target micropollutants in the feed and final concentrate products over different ED treatments are presented in the supplementary information (Table SI2).

[Figure 3 to be put here from a separate Figures document]

Fig. 3 Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, grey data series) and final concentrate product (right vertical axis, black patterned data series) in the ED treatment 1 (target micropollutant concentration of 10 µg/L). (n=3, error bars = 95% confidence interval).

[Figure 4 to be put here from a separate Figures document]

Fig. 4 Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, dark grey (treatment 2) and light grey (treatment 3) data series) and final concentrate product (right vertical axis, black patterned (treatment 2) and dark grey patterned (treatment 3) data series) in the ED treatment 2 (micropollutant concentration of 100 µg/L) and 3 (micropollutant concentration of 100 µg/L, strong initial product). (n=3, error bars = 95% confidence interval)

Overall, less than 8% from the pollutants present in the dilute feed solutions was transported to the final concentrate product in the ED treatments conducted (Table 4). Thus, over 92% retention of all target pollutants, calculated as a percentage of the feed micropollutant amount (µg) retained by the ion exchange membranes, was achieved in the ED experiments.

Table 4 Average percentage of the target pollutants transported from the dilute feed solution to the final concentrate product in the 8 h ED treatments. (n=3, 95% confidence interval given in brackets).

[Table 4 to be put here from a separate Tables document]

On average the atenolol, metoprolol, hydrochlorothiazide and trimethoprim (Fig. 3 and 4, Table 4) had the highest tendency to move across the ion exchange membranes to the concentrate product. Out of these pollutants the atenolol and metoprolol were both positively charged and also relatively hydrophilic (Table 2), especially in the case of atenolol (log K_{ow} value 0.16). Hydrochlorothiazide and trimethoprim were negatively charged at the feed pH of 8.5, but both are hydrophilic (log K_{ow} -0.07 and 0.91). Diclofenac, ibuprofen, furosemide and carbamazepine were all retained efficiently in the ED experiments by ion exchange membranes (Fig. 3 and 4, Table 4). Diclofenac, ibuprofen and furosemide were all negatively charged and especially diclofenac and ibuprofen were very hydrophobic (Table 4), whereas the carbamazepine was positively charged at pH 8.5, but had relatively high log K_{ow} value (2.5). Thus, based on these results the hydrophobicity/hydrophilicity had a strong influence on the micropollutant transport through the ED membranes, but also charge had some influence on the transport. The result that some transport

394 of both positively and negatively charged pollutants occurred (transport both across the anion and
395 cation exchange membranes) during ED experiments highlighted the influence of molecule
396 hydrophobicity/hydrophilicity to the micropollutant transport.

397 Pronk et al. (2006) studied the removal of micropollutants from anthropogenic urine with
398 ED and concluded that the removal of micropollutants with ED was determined by a combination
399 of adsorption (effected highly by molecule hydrophobicity/hydrophilicity), diffusion, sieving and
400 electrostatic interactions. However, unlikely as observed by Pronk et al. (2006), the sieving and
401 diffusion did not have such a strong role in the micropollutant removal with ED based on the
402 results and micropollutant properties (Fig. 3 and 4, Table 2 and 4). No clear effect of pollutant
403 molecule size to the micropollutant transport was noticed and the initial micropollutant
404 concentration did not have a significant effect on the micropollutant transport through the ion
405 exchange membranes (Fig. 3 and 4, Table 4). Thus, the micropollutant transport through the ion
406 exchange membranes was dominated by other factors, such as adsorption,
407 hydrophobicity/hydrophilicity and electrostatic interactions. Pronk et al. (2006) also estimated that
408 the long-term operation of ED without significant permeation of micropollutants to the concentrate
409 product is possible, if the micropollutant concentrations in the feed are close to environmental
410 concentrations. Based on this study this is true for most of the target pollutants studied, however
411 some permeation of micropollutants such as atenolol and metoprolol were observed already within
412 8 h ED operating time even though the dilute feed micropollutant concentration was only 10 µg/L
413 (Table 4).

414 When considering the utilization of final concentrate product for fertilizer application the
415 final concentration of few pollutants, being atenolol (10.3 µg/L), metoprolol (9.4 µg/L),
416 hydrochlorothiazide (8.6 µg/L) and trimethoprim (9.8 µg/L), in the concentrate product was

417 significant in ED treatment 1, when considering the threshold values 0.1 and 0.01 µg/L for
418 pharmaceuticals in surface waters set by US food and drug administration and European medicine
419 agency (Besse and Garric 2008). However, the actual concentration of these pollutants in the real
420 anaerobic wastewater treatment plant effluents would be expected to be an order of magnitude
421 lower (Gao et al. 2016, Zhu et al. 2014) and dose of concentrate would be relatively low in
422 comparison with irrigation water. Further treatment of the concentrate product might still be
423 required before utilization, if wastewater was treated with ED then resultant concentrate product
424 might contain significant amount of these pollutants. Although due to the highly concentrated
425 nature of the concentrate product large dilutions would be required for application as a fertilizer,
426 significantly reducing the concentration of ammonia and micropollutants for application purposes.

427 **3.3 Adsorption of micropollutants**

428 Mass balances calculated for target pharmaceuticals indicated that either adsorption or
429 degradation of some pharmaceuticals occurred during short term ED experiments. The
430 micropollutant amount for metoprolol, trimethoprim, diclofenac and furosemide was on average
431 6-17% lower at the end of 8 h ED experiments compared to the initial amount in the dilute feed.
432 Adsorption to the ED membranes was major reason for pharmaceutical mass loss for pollutants
433 atenolol, metoprolol and furosemide in the extended 24 h ED experiment, since the missing
434 amount of these pollutants was completely desorbed to the desorption solution after 24 h
435 desorption time (Table 5). A 2 h desorption time was able to desorb almost completely these
436 pollutants from the ED membranes. For the trimethoprim and diclofenac potentially, some minor
437 degradation occurred also during ED experiments, since only limited desorption occurred during
438 desorption period (Table 5). Limited desorption for diclofenac was unexpected based on the

439 excellent results (complete desorption) obtained by Laundry and Boyer (2013) in desorption of
440 diclofenac from anion exchange membranes.

441 Panasiak et al. (2011), who studied the removal of endosulfan with ED, identified losses to
442 equipment, volatilization and degradation during the ED treatment or desorption as potential
443 reason for micropollutant mass loss in addition to possible adsorption. However, losses to the ED
444 equipment can be minimized by using glass and stainless-steel equipment and sample vials instead
445 of polymeric material such as polystyrene (Panasiak et al. 2011). Micropollutant endosulfan losses
446 to the equipment was not significant in the study made by Panasiak et al. (2011). Volatilization of
447 micropollutants from aqueous media depends on the water solubility and volatility of the
448 substances. Thus, small amounts of volatilization during ED can be possible for pollutants with
449 high volatility. (Panasiak et al. 2011) Therefore, potentially small part of the trimethoprim and
450 diclofenac was either degraded during ED or potentially even slightly volatilized. However major
451 part was presumably very strongly adsorbed to the ED membranes and could not be desorbed with
452 the used solution and desorption time of 24 h.

453 Table 5 Percentage pollutant mass loss in the 24h ED experiment with a pollutant concentration of 100 µg/L
454 and in the 24h desorption experiment as well as desorption efficiencies.

455 [Table 5 to be put here from a separate Tables document]

456 Pronk et al. (2006) concluded an adsorption to the ED membranes as one of the major
457 removal mechanisms of micropollutants when anthropogenic urine was treated with ED. In their
458 study, the tendency of adsorption increased in the following order: carbamazepine, ibuprofen,
459 propranolol and diclofenac. Electrostatic interactions and especially hydrophobicity was identified
460 to have a major role in the adsorption behavior. Diclofenac was observed to adsorb the most to the
461 ED membranes, potentially due to high hydrophobicity. (Pronk et al. 2006) Similar observation
462 about the factors effecting adsorption could be done in this study, since the beta blockers atenolol

463 and metoprolol (adsorption mainly due to electrostatic interactions) as well as anti-inflammatory
464 drug diclofenac (adsorption mainly due to hydrophobicity) had a clear tendency for adsorption,
465 whereas the carbamazepine and ibuprofen did not show pronounced tendency for adsorption.
466 Pronk et al. (2006) also studied desorption of micropollutants from ED membranes after long term
467 experiments (90 days) by current reversal as well as by incubating ED membranes in a specific
468 scintillation-counter cocktail to release the micropollutants from membranes. Current reversal was
469 concluded to be slow and inefficient desorption method; only 34% of the adsorption could be
470 released from the membranes after 840 h of current reversal. After an incubation period of 1000 h
471 a total of 93% of the adsorbed micropollutants had been released from the membrane (Pronk et al.
472 2006).

473 Desorption of micropollutants from ED membranes can thus be a slow process and
474 complete desorption might be challenging to achieve. According to the results of this study and
475 findings from the literature (Pronk et al. 2006) especially hydrophobic pollutants such as
476 diclofenac can adsorb strongly to the ED membranes. The adsorption of diclofenac could not be
477 distinguished between AEM and CEM membranes with the arrangement of the desorption study.

478 ## 4 Conclusions

479 The transport of pharmaceuticals during ED treatment of wastewater was studied in this
480 work. The aim was to examine if the pharmaceuticals ability to transport across the ion exchange
481 membranes and eventually concentrate into the concentrate product.

482 Laboratory scale ED was able to concentrate nutrients such as NH_4^+-N, PO_4^{3-}-P and K^+ up
483 to 5 times (3700-4000 mg/L NH_4^+-N, 21-25 mg/L PO_4^{3-}-P, 990-1040 mg/L K^+). Less than 8% of
484 the pollutants present in the dilute feed solutions were transported to the final concentrate product
485 in the ED treatments conducted in this study. For many target pollutants, such as diclofenac,

carbamazepine, furosemide, ibuprofen and caffeine, the transport extent was less than 1%. However, a small accumulation of atenolol and metoprolol as well as proportioning of micropollutants trimethoprim and hydrochlorothiazide was observed during ED experiments. These pollutants however are present in an order of magnitude lower than concentrations in the real wastewaters, and the ED concentrate product would be diluted before potential utilization as fertilizer. Thus, this study indicates that the ED can produce safe concentrate product for use as a fertilizer, which contains non-effective concentrations of studied micropollutants.

Transport of pharmaceuticals across the ED membranes depended largely on molecule hydrophobicity/hydrophilicity but also on electrostatic interactions between pharmaceutical molecules and ED membranes. Target pollutants having a negative charge at present pH conditions and high hydrophobicity such as diclofenac and ibuprofen were preferentially retained in the diluent. Further work with real wastewaters is required to confirm the observations of this study and to examine if ED can also retain other micropollutants to enable production of a concentrate product suitable for fertilizer purposes.

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Figures in manuscript WR48518

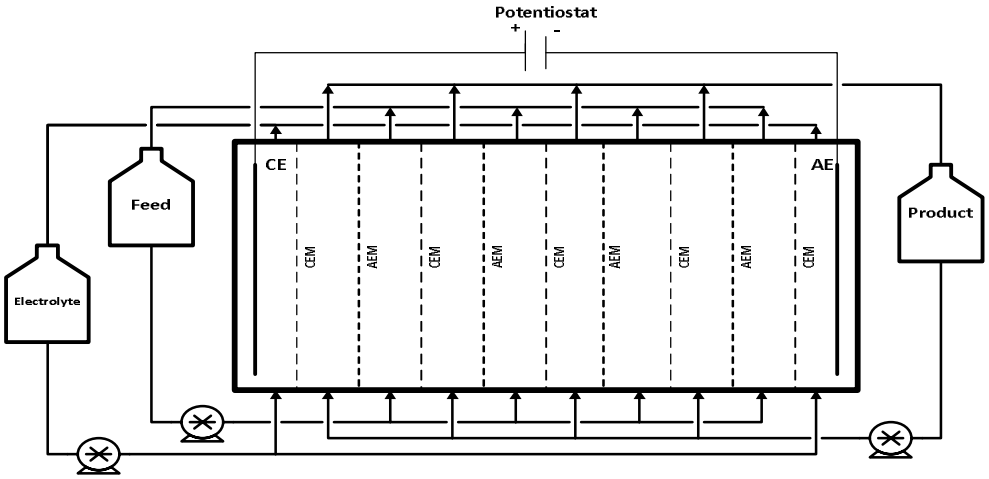

Fig. 1 Schematic diagram of the used ED setup.

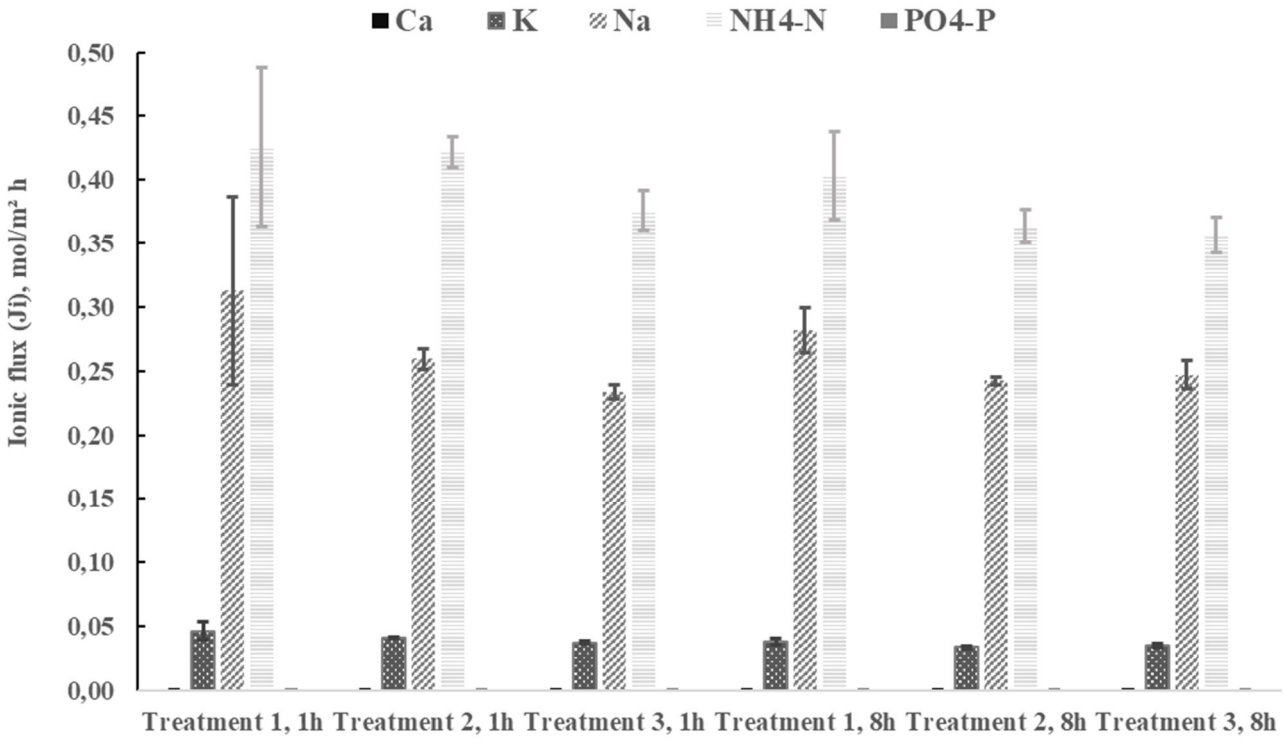

Fig. 2 Average ionic fluxes (J_i, mol/m^{2}h) for the 1 and 8-hour operating periods in the triplicate ED experiments with a dilute feed micropollutant concentrations of 10 (treatment 1) and 100 µg/L (treatment 2) as well as in the experiments with strong initial product (treatment 3). ED operated 8h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min. (n=3, error bars = 95% confidence interval).

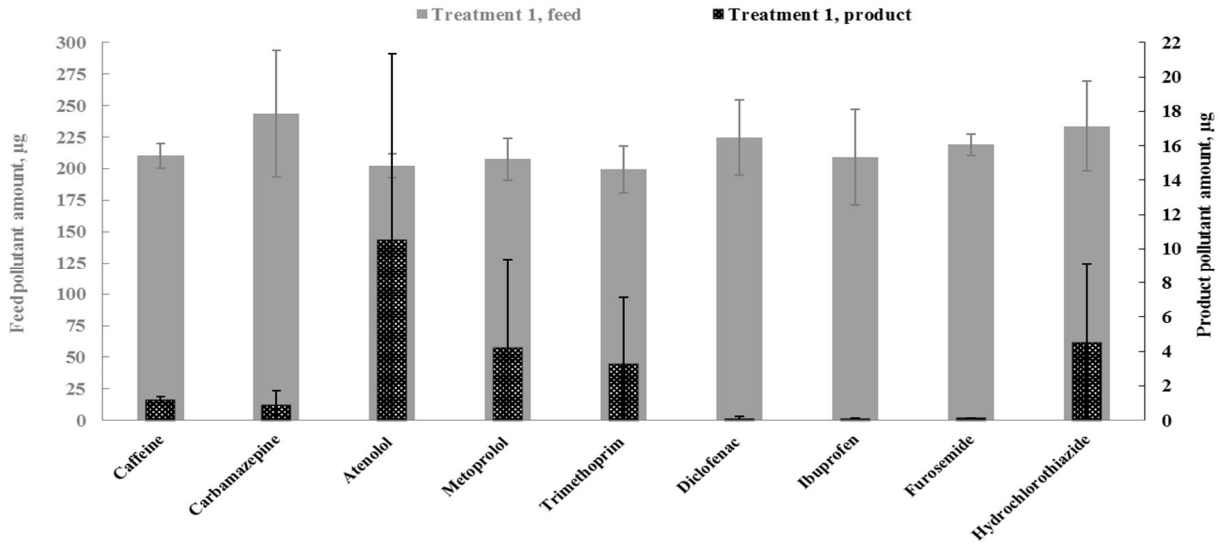

Fig. 3 Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, grey data series) and final concentrate product (right vertical axis, black patterned data series) in the ED treatment 1 (target micropollutant concentration of 10 µg/L). (n=3, error bars = 95% confidence interval).

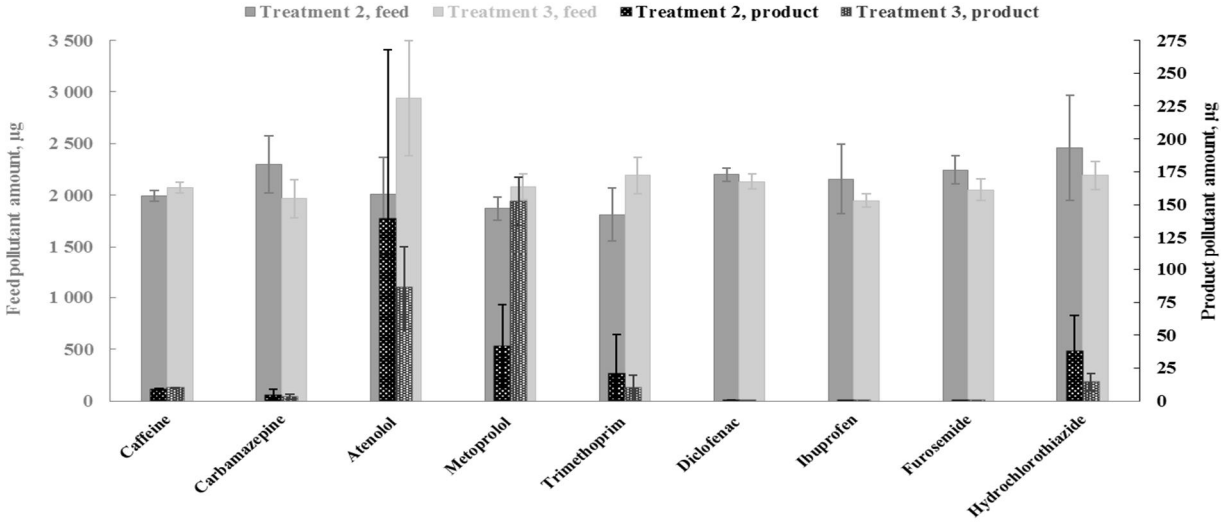

Fig. 4 Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, dark grey (treatment 2) and light grey (treatment 3) data series) and final concentrate product (right vertical axis, black patterned (treatment 2) and dark grey patterned (treatment 3) data series) in the ED treatment 2 (micropollutant concentration of 100 µg/L) and 3 (micropollutant concentration of 100 µg/L, strong initial product). (n=3, error bars = 95% confidence interval)

Tables in the manuscript WR48518

Table 1 Average properties of synthetic wastewater used as dilute feed stream in ED experiments.

Parameter	Concentration, mg/L	Added as
NH_4^+-N	756 (738-784)	NH_4Cl, $NH_4H_2PO_4$
Na^+	933 (912-982)	$NaHCO_3$, NaCl, NaOH
K^+	196 (192-203)	K_2SO_4
Ca^{2+}	4.6 (4.5-4.8)	$CaCl_2 \cdot 2H_2O$
PO_4^{3-}-P	4.8 (4.4-5.2)	$NH_4H_2PO_4$

Table 2 Molecular characteristics of the studied micropollutants and their concentrations in the ED dilute feed stream (pH 8.5).

Micropollutant	**Classification**	**Formula**	**Molar mass, g/mol**	**pKa, -**	**log K_{ow}, -**	**Charge at pH 8.5**	**Feed concentration, µg/L**
Ibuprofen	Pain killer	$C_{13}H_{18}O_2$	206.3[a]	4.9[a]	4.0[a]	negative	10.5 (9.4-12.4) 103 (94-123)
Diclofenac	Non-steroidal anti-inflammatory drug	$C_{14}H_{11}Cl_2NO_2$	296.2[a]	4.2[a]	4.5[a]	negative	11.3 (9.8-12.1) 108 (103-113)
Carbamazepine	Anti-epileptic agent and mood stabilizer	$C_{15}H_{12}N_2O$	236.3[a]	13.9[a]	2.5[a]	positive	12.2 (9.7-13.8) 107 (89-128)
Atenolol	Cardioselective beta blocker	$C_{14}H_{22}N_2O_3$	266.3[a]	9.6[a, b]	0.16[a, b]	positive	10.1 (9.7-10.6) 124 (91-166)
Metoprolol	Selective beta blocker	$C_{15}H_{25}NO_3$	267.4[a]	9.7[b]	1.9[a, b]	positive	10.4 (9.6-10.9) 99 (90-109)
Furosemide	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	330.7[a]	3.8[a]	2.0[a]	negative	11.0 (10.6-11.3) 108 (98-119)
Hydrochlorothiazide	Thiazide diuretic	$C_7H_8ClN_3O_4S_2$	297.7[a]	7.9[a]	-0.07[a]	negative	11.7 (10.7-13.5) 116 (103-147)
Trimethoprim	Antibiotic	$C_{14}H_{18}N_4O_3$	290.3[a]	7.1[a]	0.91[a]	negative	10.0 (9.0-10.5) 100 (84-116)
Caffeine	Central nervous system stimulant	$C_8H_{10}N_4O_2$	194.2[a]	14.0[a]	-0.07[a]	positive	10.5 (10.2-11.0) 102 (97-105)

Data obtained from [a]PubChem Open chemistry database 2017, [b]Maurer et al. (2007)

Table 3 Average concentrations of NH_4^+-N, PO_4^{3-}-P, K^+ and Ca^{2+} in the ED dilute feed and final concentrate products as well as their concentration factors during ED experiments. ED operated 8h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min. (n=3).

		Treatment 1 (10 ug/L)	**Treatment 2 (100 ug/L)**	**Treatment 3 (100 ug/L with strong initial product)**
Feed concentration, mg/L	**NH_4^+-N**	747	768	5510
	PO_4^{3-}-P	5.1	4.6	27
	K^+	198	193	1513
	Ca^{2+}	4.6	4.5	44
Final concentration in product, mg/L	**NH_4^+-N**	3692	3957	5723
	PO_4^{3-}-P	25	21	27
	K^+	1038	987	1587
	Ca^{2+}	22	22	44
Concentration factor, -	**NH_4^+-N**	4.9	5.2	1.0
	PO_4^{3-}-P	4.9	4.5	1.0
	K^+	5.2	5.1	1.0
	Ca^{2+}	4.7	4.8	1.0

Table 4 Average percentage of the target pollutants transported from the dilute feed solution to the final concentrate product in the 8 h ED treatments. (n=3, 95% confidence interval given in brackets).

	Percentage of pollutant in the final concentrate product from the initial feed								
Treatment	Caffeine	Carbamazepine	Atenolol	Metoprolol	Trimethoprim	Diclofenac	Ibuprofen	Furosemide	Hydrochlorothiazide
1 (10 ug/L)	0.57% (0.08)	0.32% (0.33)	5.3% (5.6)	2.0% (2.4)	1.6% (1.9)	0.04% (0.05)	0.04% (0.006)	0.06% (0.003)	1.9% (2.2)
2 (100 ug/L)	0.45% (0.03)	0.22% (0.21)	6.5% (5.2)	2.2% (1.7)	1.2% (1.8)	0.01% (0.01)	0.004% (0.0007)	0.0059% (0.0001)	1.7% (1.3)
3 (100 ug/L + strong initial product)	0.49% (0.03)	0.17% (0.08)	2.9% (0.9)	7.4% (1.1)	0.4% (0.4)	0.00053% (0.0006)	0.004% (0.008)	0.009% (0.006)	0.7% (0.3)

Table 5 Percentage pollutant mass loss in the 24h ED experiment with a pollutant concentration of 100 µg/L and in the 24h desorption experiment as well as desorption efficiencies.

Mass balance	**Percentage pollutant mass loss, %**				
	Atenolol	**Metoprolol**	**Trimethoprim**	**Diclofenac**	**Furosemide**
Initial vs after 24h ED experiment	42	52	51	37	29
Initial vs 2h desorption	12	17	47	35	0
Initial vs 24h desorption	-3	-6	48	35	-7
Desorption efficiency	**Recovered mass from total adsorbed mass, %**				
2h desorption	71	68	7	6	102
24h desorption	108	111	5	6	125