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Fate of pharmaceuticals and PFASs during the electrochemical generation of a nitrogen-rich nutrient product from real reject water

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ABSTRACT

Recycling vital macronutrients, such as nitrogen, from wastewaters back to fertiliser use is becoming essential to ensure sustainable agricultural practices. Technologies developed for such purposes are typically evaluated for their capacity to recover nutrients; however, the presence of contaminants of emerging concern (CECs) in these waste-derived nutrient products must not be overlooked. In this study, nitrogen was recovered from real anaerobically digested municipal sewage sludge reject water using a novel set-up combining membrane-based electroconcentration (EC) with electrochemical advanced oxidation processes (EAOPs). Simultaneously, the fate of five spiked pharmaceuticals (carbamazepine, ciprofloxacin, diclofenac, erythromycin and metoprolol) as well as ten indigenous perfluoroalkyl substances (PFASs) was investigated. The EC-EAOP system was effective in up-concentrating nitrogen ca. 13 times to a final concentration of 12.7 ± 0.8 g L^{-1} in the nutrient product. At the same time, no up-concentration was observed for the pharmaceuticals and their concentrations in the recovered concentrated remained at $\leq 3.4 \pm 1.3$ μg L^{-1}. The EAOPs were the main transformation mechanism for all the pharmaceuticals at 33–88% efficiency, while diclofenac also notably adsorbed in the system (30 ± 1.4%). Out of the ten studied PFASs, only three were found in the recovered nutrient concentrate, albeit at very limited concentrations of $\leq 0.024 \pm 0.013$ μg L^{-1}. The EAOPs were found to degrade longer-chain PFASs into their shorter-chain counterparts. The low contaminant concentrations in the nutrient product pose a reduced risk for soil contamination compared to, e.g., biosolids that are more typically used as fertilisers.

1. Introduction

The growing need for ammonium nitrogen (NH_4-N) fertilisers in agriculture combined with the environmental issues related to their production [1] advocate more efficient NH_4-N recycling and reuse. Currently, up to 30% of NH_4-N used in fertilisers ends up in municipal wastewaters [1–3], which are typically collected and centrally treated at wastewater treatment plants (WWTPs). At conventional WWTPs, the most nitrogen-rich streams (ca. 1 $g_{NH4\text{-}N}$ L^{-1}) are the reject waters [4,5], i.e., the liquid fraction originating from the dewatering of anaerobically digested sewage sludge. Reject waters have therefore gained interest as potential sources for nitrogen recovery via, e.g., struvite precipitation [6,7], nanofiltration [8] or various (bio)electrochemical methods [4, 9–14]. A promising option for NH_4-N recovery from reject waters is (bio) electroconcentration ((B)EC), which was recently shown to achieve up to 82 ± 5.7% recovery efficiency at industrially applicable rates of

Abbreviations: AD, Anaerobic digestion; AEM, Anion-exchange membrane; BDD, Boron-doped diamond; BEC, Bioelectroconcentration; CBZ, Carbamazepine, an anticonvulsant; CECs, Contaminants of emerging concern; CEM, Cation-exchange membrane; COD, Chemical oxygen demand; CPFX, Ciprofloxacin, a fluoroquinolone antibiotic; DCL, Diclofenac, an anti-inflammatory; EAOPs, Electrochemical advanced oxidation processes; EC, Electroconcentration; EC-EAOP, Electroconcentration–electrochemical advanced oxidation processes; ERY, Erythromycin, a macrolide antibiotic; IEM, Ion-exchange membrane; MQ, Milli-Q water; MTP, Metoprolol, a selective beta-blocker/antiarrhythmic agent; PFAS, Per- or polyfluoroalkyl substance; POP, Persistent organic pollutant; WWTP, Wastewater treatment plant.

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1.3–4.4 $kg_N\ m^{-3}\ d^{-1}$ from real municipal reject water [10].

When employing such processes for the efficient recovery of key nutrients, the potential co-recovery of contaminants in the products must also be considered. These include contaminants of emerging concern (CECs), such as pharmaceutical residues, which are resistant to biodegradation by design, and therefore pass through human bodies and WWTPs virtually unchanged [15–17]. At the same time, many CECs are reported to be bio-accumulative and toxic to different organisms [16,18]. For example, the anti-inflammatory diclofenac has been found to cause immediate alterations in fish kidneys and gills already at low concentrations (5 μg L^{-1}) and accumulate in several fish organs, suggesting a general impairment of fish health after prolonged exposure to diclofenac [18]. Furthermore, exposure to the antibiotic ciprofloxacin has been found to cause shifts in the microbial communities in the microbial processes of WWTPs, potentially promoting the spread of antibiotic-resistant strains [19]. As a result, e.g., the European Union (EU) has included several pharmaceuticals, such as the antibiotics ciprofloxacin and erythromycin, on a watch list of contaminants that are suspected to pose a risk to or via the aquatic environment but require further monitoring data for a detailed risk evaluation [20,21]. Meanwhile, there have been suggestions to include several pharmaceutical compounds, such as carbamazepine, diclofenac and metoprolol, as markers for the efficiency of water treatment in Switzerland [22].

Another class of CECs are per- and polyfluoroalkyl substances (PFASs), which comprise several thousand different synthetic chemicals that have been used for decades in different consumer and industrial applications, such as coatings and water repellents, fire-fighting foams, and lubricants [23,24]. However, concerns have arisen regarding the ubiquitousness of PFASs found in the environment and biota, and their reported persistence, toxicity and bioaccumulation [25–27]. For example in the EU, these concerns have led to the listing of the most commonly used PFASs, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), as persistent organic pollutants (POPs), whose manufacturing and use were consequently prohibited [28,29]. Currently, however, both PFOS and PFOA together with other PFASs are still globally detected in municipal wastewaters, typically in the 10^1–10^2 ng L^{-1} range [30–33].

Due to their persistent nature, CECs are very resistant to current wastewater treatment processes. Therefore, they typically partition between the effluent water and the sewage sludge generated in the treatment process depending on their physico-chemical characteristics, such as hydro-/lipophilicity and charge [34]. Generally, lipophilic compounds are subject to sorption into biosolids more readily [15,35,36]. During anaerobic digestion (AD) of the sewage sludge, further changes in the solid–liquid distribution have been observed [37], which determine whether certain compounds eventually end up in the dewatered digestate or reject water. So far, most studies examining the distribution of CECs within WWTPs have focused on the influent and effluent waters, the sewage sludge before/after AD or the solid fraction after sludge dewatering [30,31,38], whereas reject waters (that are typically simply recirculated back to the wastewater treatment process) have received less attention. Nevertheless, several pharmaceutical contaminants have also been detected in reject waters at municipal WWTPs, typically in the ng L^{-1} to μg L^{-1} range [37,39–41]. Less monitoring data is available for PFASs, but theoretical calculations [42] and laboratory partitioning tests [43] suggest PFASs presence in reject waters in the tens of ng L^{-1} range, making it clear that CECs need to be considered when recovering nitrogen from reject waters.

So far, few studies have examined the presence of CECs in nutrient products derived from reject waters [6–8,14]. Even if the studied processes have been effective in rejecting ca. 75–100% of the CECs from the nutrient product, they have merely removed the contaminants via membrane exclusion or phase transition without altering them. Thus, the remaining CECs-containing liquid streams still require further treatment. Furthermore, all these studies have focused on pharmaceutical compounds, with no information about the presence of PFASs in reject water-derived nutrient products.

In this study, the production of a nitrogen-rich, CECs-free nutrient product from real reject water was investigated using a novel EC-EAOP system [10] combining membrane-based electroconcentration (EC) with the use of a boron-doped diamond (BDD) electrode that facilitated electrochemical advanced oxidation processes (EAOPs). In EAOPs, hydroxyl (and potentially other) radicals capable of oxidising CECs are created in situ using electrical energy [44]. In the present study, the aim was therefore to both exclude the CECs from the produced liquid nutrient product by the ion-exchange membranes (IEMs) and to mineralise them with the EAOPs within the same process step. In addition to selected spiked pharmaceuticals, the presence of ten indigenous PFASs in the real reject water and their fate in the EC-EAOP system was determined.

2. Materials and methods

2.1. Studied pharmaceuticals and PFASs

Five pharmaceutical compounds with different uses were selected to study their fate in the EC-EAOP unit (for operational details, see Section 2.3 and Koskue et al. [10]): the anticonvulsant carbamazepine (CBZ); the fluoroquinolone antibiotic ciprofloxacin (CPFX); the anti-inflammatory diclofenac (DCF); the macrolide antibiotic erythromycin (ERY); and the selective beta-blocker/antiarrhythmic agent metoprolol (MTP) (Table 1). The physico-chemical properties of the selected compounds are described in more detail in Table SA.1 and Figs. SA.1 and SA.2 in Supplementary Material.

Native standards of carbamazepine, ciprofloxacin, diclofenac (sodium salt), erythromycin and metoprolol (tartrate salt) (Sigma-Aldrich, USA) were used for reject water spiking at concentrations outlined in Table 1, set close to the maximum values reported in literature for reject waters. For spiking, a 100-times concentrated mixed stock solution was prepared in methanol. Corresponding deuterated standards carbamazepine-d8 (major), ciprofloxacin-d8, diclofenac-d4, erythromycin-c13,d3 and metoprolol-d6-hemi(+)-tartrate (Toronto Research Chemicals, Canada) were used as internal standards (more details in Table SB.1). Mixed stock solutions containing 1 and 10 ppm of all the deuterated standards were prepared in methanol.

In addition, the presence of ten different commonly used and nowadays largely regulated PFASs [24,45] was examined from the reject water used as the feed to the experimental unit (for details, see Section 2.2), as well as samples collected from the system effluent and produced concentrate at the end of the experimental run. Contrary to the pharmaceuticals, no additional PFASs were spiked into the reject water feed. The analysis was carried out for seven perfluorinated carboxylic acids (PFCAs; C_4–C_{10}) PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA, and three perfluorinated sulfonic acids (PFSAs; C_4, C_6, C_8) PFBS, PFHxS and PFOS (for details, see Table SA.2). A 0.2 ppm mixed stock solution of the corresponding internal standards $^{13}C_4$-PFBA, $^{13}C_4$-PFPeA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_3$-PFBS, $^{18}O_2$-PFHxS and $^{13}C_4$-PFOS (Wellington Laboratories, Canada) was prepared in methanol and used in the analysis detailed in Section 2.6. All standards and chemicals used were of analytical grade.

2.2. Real reject water and pharmaceutical spiking

Real reject water was used as feed to the experimental unit in all experiments (Sections 2.4 and 2.5). The reject water was collected after centrifugation of the anaerobically digested sewage sludge at Luggage Point WWTP (Brisbane, Australia) and stored at + 4 °C for a maximum of one week. To avoid blockages in the operational set-up, the solids were allowed to settle in the storage canisters and the supernatant was decanted into a feed bottle. The decanted reject water contained on average (in mg L^{-1}): NH_4-N (977 ± 39), PO_4-P (7.3 ± 1.9), K (221 ± 11), Na (341 ± 19), Ca (36 ± 4), Mg (18 ± 7), Cl (656 ± 25), inorganic carbon

Table 1
List of the studied pharmaceutical compounds, their uses, and the concentrations they were spiked at, based on the concentrations in reject waters reported in the literature.

Compound	Use	Spiked concentration [μg L^{-1}]	Concentrations in literature [μg L^{-1}]	References
Carbamazepine (CBZ)[a]	Anticonvulsant	15	0.2–0.3	[36]
			0–16	[41][b]
			0.07–0.18	[37]
Ciprofloxacin (CPFX)[c]	Antibiotic (fluoroquinolone)	5	0–7	[41][b]
			0.1–0.45	[37]
Diclofenac (DCL)[a]	Anti-inflammatory	15	0–15	[41][b]
			0.08–0.4	[37]
Erythromycin (ERY)[c]	Antibiotic (macrolide)	1	0.02–0.94	[37]
Metoprolol (MTP)[a]	Selective beta blocker/anti-arrhythmic	15	0–15	[41][b]
			0.01–0.02	[37]

[a] Proposed marker compound for wastewater treatment efficiency monitoring in Switzerland [22].
[b] Values from both 100% sewage sludge digestion and co-digestion with other waste materials.
[c] Included in the EU watch list of contaminants for union-wide monitoring [20].

(685 ± 34), acetate (265 ± 32) and propionate (49 ± 6). The total organic content of the reject water, expressed as chemical oxygen demand (COD), ranged from 442 to 1265 mg L^{-1} [10].

A fresh batch of reject water was collected from the cold storage daily, spiked with the native pharmaceutical stock solution (at 1:100 ratio), mixed with a magnetic stirrer for 15 min to ensure even distribution of the contaminants in the solution, and used as feed at room temperature for a maximum of 24 h.

2.3. Reactor set-up

The experiments were carried out in duplicate lab-scale reactors consisting of an EC-EAOP unit and an additional stripping unit (for stripping volatile ammonia gas), as previously reported by Koskue et al. [10]. Due to the low Henry's law constant (K_H) values of $\leq 1.08 * 10^{-7}$ atm m^3 mol^{-1} for all the studied pharmaceuticals (Table SA.1) and estimated values ≤ 0.017 atm m^3 mol^{-1} for the PFASs (Table SA.2), volatilisation of these compounds in the ammonia gas stripping column was not expected to take place and the CECs were not analysed from the absorption column. Thus, the focus of the present study was on the EC-EAOP unit (Fig. 1).

Briefly, the three-chamber EC-EAOP unit with an anode, concentrate and cathode chamber was constructed using a cation- (CEM; CMI-7000, Membranes International, USA) and an anion-exchange membrane (AEM; AMI-7100, Membranes International, USA). The hydraulic volumes of the two reactors were 125 ± 3 mL for the anode, 118 ± 6 mL for the cathode and 78 ± 0 mL for the middle chamber. A 40.5 cm^2 DIACHEM® boron-doped diamond (BDD) electrode (Condias GmbH, Germany) connected to a stainless-steel or niobium rod was used as the anode and a 100 cm^2 piece of AISI 316 L stainless steel sintered fibre felt (Xinxiang Lier Filter Technology Co. Ltd, China) with titanium wire as current collector was used as the cathode.

All experiments were conducted at room temperature (22 ± 2.5 °C) and the reactor set-up including feed, concentrate and effluent bottles was protected from light with foil coverings. Peristaltic pumps (Sci-Q 323, Watson-Marlow Fluid Technology Group, United Kingdom) were used for both liquid and gas pumping. The reactors were dismantled between different experiments and all parts carefully cleaned by scrubbing with soapy water, followed by rinsing with methanol and Milli-Q (MQ) water to remove any CECs traces.

2.4. Control experiments in open circuit

Before investigating the fate of the CECs in the EC-EAOP unit under normal operation, two control experiments were carried out under open circuit voltage (i.e., no electric current/voltage was applied) to study the potential diffusion of the five pharmaceutical compounds through the IEMs without an electric driving force. Both control experiments were carried out as 24-h tests and the concentrate chambers were initially filled with concentrate produced from synthetic reject water in an

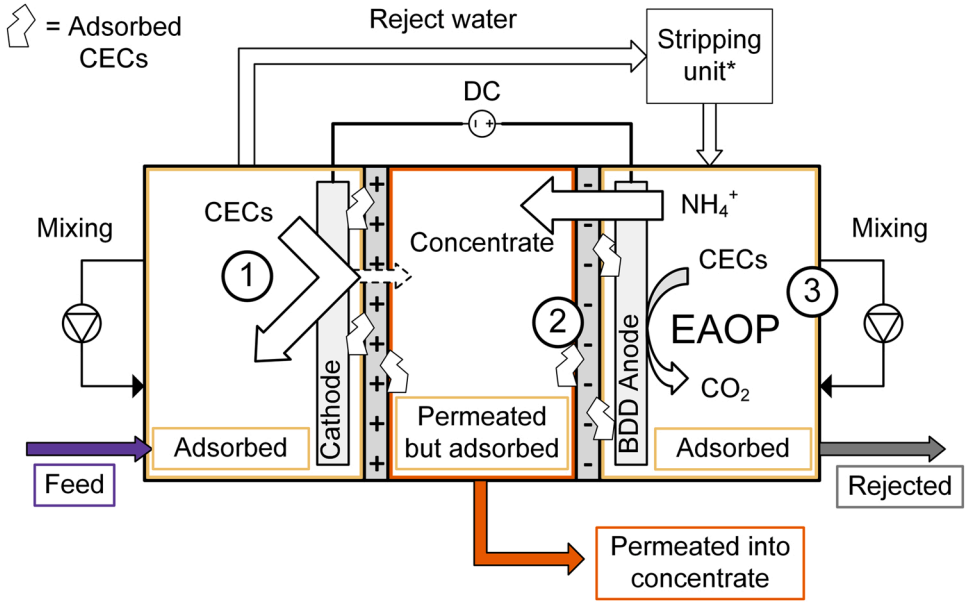

Fig. 1. Summary of the studied system boundaries and relevant in- (feed) and outflows (concentrate and effluent, i.e., 'rejected') as well as the expected contaminants of emerging concern (CECs) removal mechanisms in the three-chamber EC-EAOP unit. The CECs were expected to (1) be largely retained by the ion-exchange membranes with little permeation into the concentrate chamber; (2) adsorb in the system, especially on the charged membrane surfaces [46]; and (3) be mineralised at the boron-doped diamond (BDD) anode as a result of electrochemical advanced oxidation processes (EAOPs). *As explained in Section 2.3, the stripping unit was not considered to contribute to the removal of pharmaceuticals and PFASs and was therefore not examined in this study.

earlier experiment in the same experimental unit (experiment S1 as reported before by Koskue et al. [10]), diluted 1:1 (v/v) with MQ. The concentrates originated from synthetic reject water to ensure no CECs were present in the concentrate chamber in the beginning of the experiments.

In the first open-circuit control experiment (OC), the EC-EAOP unit was operated identically to the closed-circuit run (see Section 2.5 and Koskue et al. [10]), but no electric current was applied. The spiked reject water pH was not altered and remained stable at 8.3. At the end of the experiment, triplicate 50 mL samples were collected from the feed ($n = 3$) and effluents ($n = 6$) and duplicate 30 mL samples (due to limited volume) from the concentrates ($n = 4$) for the pharmaceutical analysis, together with ca. 5 mL samples for NH_4-N ($n = 2$; for details on sample preparation and analyses, see Section 2.6).

In the second open-circuit control experiment (OC–pH), the anode and cathode chambers were fed separately with the spiked reject water at 0.8 L d^{-1} each. Furthermore, the anodic feed pH was adjusted to 5.1 with 5 M HCl and the cathodic feed pH to 10.3 with 5 M NaOH. These pH values aimed to replicate the reject water pH in the anode and cathode chambers under closed-circuit conditions, where changes in pH occur as a result of oxidation and reduction reactions. Changes in reject water pH may result in dissociation of the pharmaceuticals depending on their pKa values (see Table SA.1 and Figure SA.1) which further affects their lipophilicity, expressed as log D (Figure SA.2). OC–pH was thereby carried out to study the diffusion of these compounds into the concentrate at the expected pH ranges without an applied current. The samples numbers and volumes were analogous to OC but this time the anodic and cathodic feeds as well as the anodic and cathodic effluents were sampled separately.

For both OC and OC–pH experiments, the reactors were emptied after sampling and known volumes of methanol were run through the system for 2 h to desorb and recover possibly adsorbed pharmaceuticals separately from the concentrate chamber and the rest of the system. After concluding the desorption, 1 mL samples were collected and analysed for the adsorbed pharmaceuticals.

2.5. Fate of CECs in the EC-EAOP unit in closed circuit

Finally, the fate of the CECs in the EC-EAOP unit was studied in continuous mode and closed circuit. The operational conditions were analogous to the NH_4-N recovery experiment R3 in Koskue et al. [10]. Briefly, real reject water spiked with the pharmaceutical compounds (see Section 2.2) was continuously fed to the cathode chamber of the electroconcentration unit at 1.5 L d^{-1}, from where it continued over the stripping column to the anode. The combined hydraulic retention time (HRT) of the cathode and anode chambers was 4.1 h. The effluent from the anode was collected into an effluent bottle and the overflow of the liquid concentrate from the middle chamber into a concentrate bottle. The concentrate chamber was initially filled with concentrate generated in an earlier experiment with synthetic reject water, diluted 3:1 (v/v) with MQ. The catholyte and anolyte were circulated in the respective chambers at 50.4 L d^{-1} to reduce mass transfer limitations. A laboratory DC power supply (IPS 2303, ISO-TECH) was used to apply a constant current of 0.35 A, corresponding to a current density of ca. 86 A m^{-2} relative to anode surface area (or 35 A m^{-2} to effective membrane surface area).

The reactors were operated for five days until they reached a steady state (i.e., variations in the electric conductivity of the concentrate were $< 5\%$). During steady state, triplicate 50 mL samples were taken from the feed ($n = 9$), triplicate 200 mL samples from the effluents (to account for the expected lower pharmaceutical concentrations; $n = 18$) and duplicate 30 mL samples from the concentrates (due to limited volume; $n = 11$) three times every 24 h for the five spiked pharmaceuticals. Simultaneously, ca. 5 mL samples were collected for NH_4-N ($n = 6$). At the end of the experiment, duplicate 50 mL samples were collected from the feed ($n = 2$) and effluents ($n = 4$) and single 50 mL samples from the concentrates ($n = 2$) for the PFASs analysis.

After concluding the sampling, a desorption solution was circulated separately through the concentrate chamber and the rest of the system to recover any adsorbed pharmaceuticals. This time, a 1:1 (v/v) methanol-MQ mix with 45 g_{NaCl} L^{-1} was used for desorption due to its better reported efficiency to desorb pharmaceuticals compared to pure methanol [47] and the solution was circulated through the system for 24 h [14]. Finally, triplicate 50 mL samples were collected from the desorption solution used for the anode and cathode chambers ($n = 6$) and duplicate 30 mL samples from the solution used for the concentrate chamber ($n = 4$) for pharmaceutical analysis. The desorption solution was not analysed for PFASs.

2.6. Sample preparation and chemical analyses

NH_4-N samples were filtered through Millex® syringe filters (pore size 0.22 μm; Merck Millipore, Germany) and stored at − 20 °C before analysis with a Flow Injection Analyser (Lachat Quikchem 8500 Series 2; Hach, USA). For details on analyses and results on other macro- and micronutrients, the reader is advised to refer to our previously published work [10].

For the pharmaceutical analysis, all samples were spiked with known concentrations of the mixed internal standard stock solution immediately after sampling and stored at − 20 °C for further processing. The pharmaceutical samples were extracted and concentrated using solid phase extraction (SPE) (except for the desorption samples from OC and OC–pH that were analysed as such) as detailed in Appendix B in Supplementary Material.

The pharmaceuticals were analysed with a Shimadzu Prominence high performance liquid chromatography (HPLC) system (Japan) coupled with an AB SCIEX QTRAP 4000 liquid chromatography–tandem mass spectrometer (LC-MS/MS) with an electrospray (ESI) probe, all controlled using SCIEX Analyst software (Canada). The LC-MS/MS was operated in multiple reaction monitoring (MRM) in both positive and negative scan mode. The results from this LC-MS/MS analysis were used for comparing the concentrations in the influent and concentrate for all the pharmaceuticals (Fig. 2 and Section 3.1), as well as for constructing mass balances for ciprofloxacin and erythromycin (Fig. 3 and Section 3.1).

In the effluent and adsorption samples, carbamazepine, diclofenac and metoprolol were present at higher concentrations than anticipated and the samples therefore needed to be diluted and re-analysed. Meanwhile, the original LC-MS/MS was no longer available, and the re-analysis was carried out with a Vanquish ultra-high performance liquid chromatograph (UHPLC) using a Kinetex C18 column (Phenomenex, USA), combined with a Q Exactive Orbitrap MS using a heated electrospray (HESI) probe (Thermo Fisher Scientific, USA). The Orbitrap MS was operated in dd-MS^2 (positive) and full MS (negative) modes. These results were used to construct mass balances for carbamazepine, diclofenac and metoprolol (Fig. 3). This second analysis was carried out ca. one year after concluding the experiments (mainly due to delays caused by the COVID-19 pandemic). It was therefore possible that some of carbamazepine, diclofenac and metoprolol had degraded in the samples over the long storage time, which is addressed further in Appendix D in Supplementary Material.

The PFAS sample preparation was conducted as previously described [48,49] with a few modifications as detailed in Appendix B in Supplementary Material. The samples were analysed with a liquid chromatograph (Shimadzu, Japan) coupled to an AB SCIEX QqQ6500+ triple quadrupole mass spectrometer (Canada), using negative electrospray ionisation run in scheduled MRM mode. A Kinetex column (2.6 μm EVO C18 100 Å, 100×2.1 mm) (Phenomenex, Australia) was used for separation and a gradient elution of mobile phase A 95% MeOH/5% Milli-Q water with 8 mM ammonium acetate and B 99% MQ water/1% MeOH with 8 mM ammonium acetate. Out of the studied ten PFAS compounds, the shortest-chain (C_4) carboxylic acid PFBA and sulfonic acid PFBS

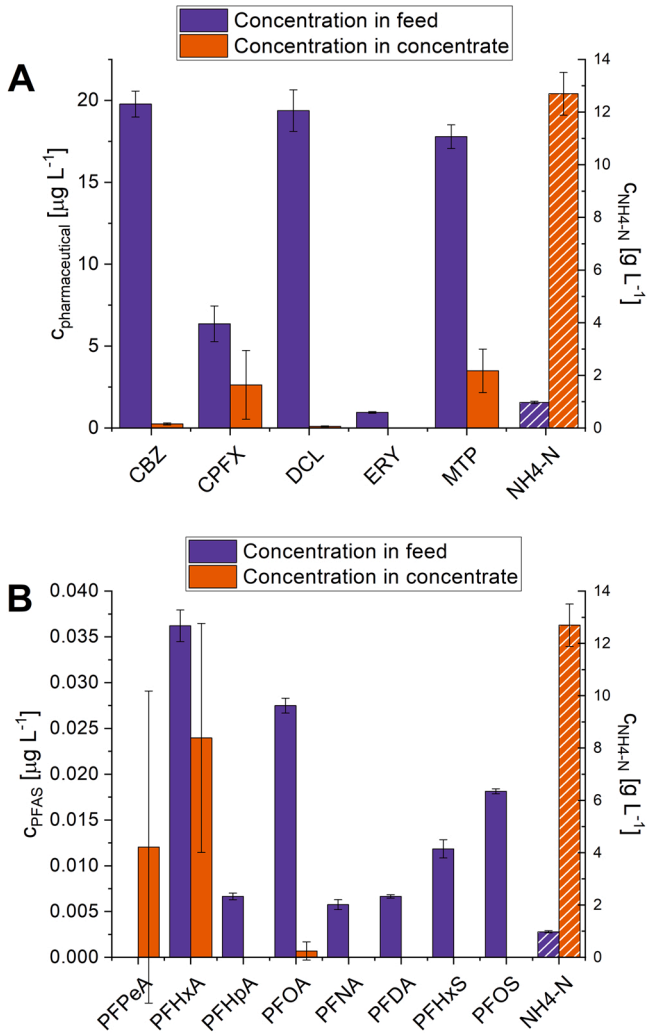

Fig. 2. Comparison of the feed (purple) and concentrate (orange) concentrations of the (A) pharmaceuticals; and (B) PFASs (solid bars; left y-axis). The concentrations are also compared to those of NH_4-N (striped bars; right y-axis). For metoprolol, the maximum calibration concentration was used for four samples that were out of calibration range. CBZ = carbamazepine; CPFX = ciprofloxacin; DCL = diclofenac; ERY = erythromycin; MTP = metoprolol.

were not detected in any of the analysed samples and were therefore excluded from the reported results.

Further details on the pharmaceutical and PFAS analytics can be found in Appendix B in Supplementary Material.

2.7. Calculations

For the pharmaceuticals and NH_4-N, the 'permeated into concentrate' fraction (Fig. 1) was calculated by comparing the concentrations in the produced concentrate and the concentrate production rate to the feed concentration and rate:

$$Permeated\ \ into\ \ concentrate\ \ (\%) = \frac{c_{i,c} * Q_c}{c_{i,f} * Q_f} \quad (1)$$

where $c_{i,c}$ is the concentration of a specific compound in the produced concentrate (µg L^{-1} or mg L^{-1}), Q_c the concentrate production rate (L d^{-1}), $c_{i,f}$ is the concentration of the same compound in the feed (µg L^{-1} or mg L^{-1}) and Q_f is the feed rate (L d^{-1}).

Similarly, the 'rejected' fraction was determined by comparing the effluent concentration and production rate to the feed concentration and rate:

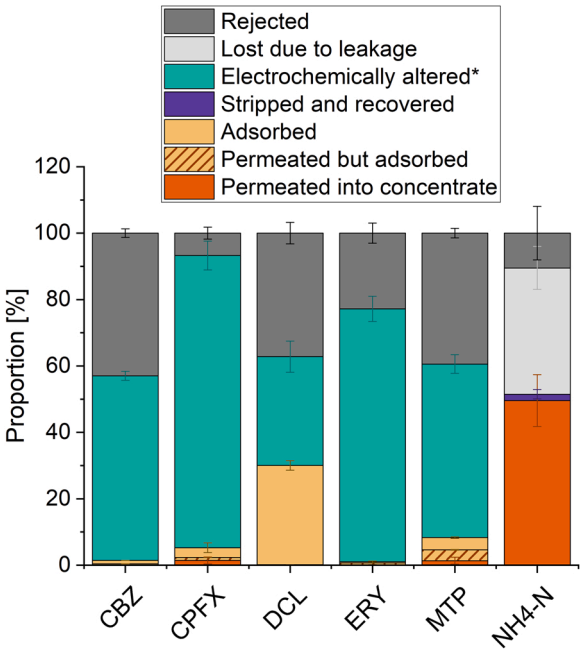

Fig. 3. Mass balances of the five studied pharmaceutical compounds as well as NH_4-N when operating the EC-EAOP unit under closed-circuit conditions. For ciprofloxacin, the adsorption efficiency was determined using the maximum concentration in the calibration curve due to the desorption sample results being out of calibration range. Unlike NH_4-N, the pharmaceuticals were not measured from the absorption column ('stripped and recovered') as explained in Section 2.3. CBZ = carbamazepine; CPFX = ciprofloxacin; DCL = diclofenac; ERY = erythromycin; MTP = metoprolol. *The 'electrochemically altered' fraction refers to the fraction not detected in any of the other outflows (concentrate, effluent or desorption solution) as explained in Section 2.7.

$$Rejected\ \ (\%) = \frac{c_{i,e} * Q_e}{c_{i,f} * Q_f} \quad (2)$$

where $c_{i,e}$ is the concentration of a specific compound in the effluent (µg L^{-1} or mg L^{-1}) and Q_e is the effluent production rate (L d^{-1}).

The 'adsorbed' fraction (as well as the 'permeated but adsorbed'; Fig. 1) was determined from the concentration measured from the desorption solution and its known volume:

$$Adsorbed\ \ or\ \ Permeated\ \ but\ \ adsorbed\ \ (\%) = \frac{c_{i,d} * V_d}{c_{i,f} * Q_{i,f} * t} \quad (3)$$

where $c_{i,d}$ is the concentration of a specific compound in the desorption solution (µg L^{-1}), V_d is the volume of the desorption solution (L) and t is the duration of the experiment (d). For the final experiment in closed circuit, the reactors were operated for several days before the steady-state sampling and adsorption was assumed to have occurred throughout the full operational period. As there were no solids, such as biomass, in the system to affect the sorption, a constant adsorption rate was assumed for all pharmaceutical compounds. Therefore, the amount adsorbed during the steady state was calculated as the share of the steady state period (3 d) of the whole operational time (7.7 d).

The 'electrochemically altered' fraction was determined as the amount fed into the reactor but not detected in any of the analysed outflows (concentrate, effluent and desorption solution; Fig. 1).

The percentual mass balances used for the pharmaceuticals were deemed unsuitable for reporting the PFAS results, mainly due to two reasons: (1) PFPeA was detected in the effluent and concentrate but was not present in the feed, which made percentual comparison based on Eqs. (1) and (2) impossible; and (2) transformations between the PFAS compounds were possible [50], leading to a potential increase in the

mass of some compounds. Therefore, the in- and outflow masses (in ng) of different PFASs in the EC-EAOP unit during the last 24 h of the closed-circuit experiment were calculated based on the feed, concentrate and effluent concentrations and the corresponding liquid flows. As the reactors were in steady state, the concentrations were assumed stable over this 24-h period.

All reported values are mean values with standard deviations (±) calculated for the sample numbers (*n*) given in Sections 2.4 and 2.5, unless stated otherwise. For statistical analyses, box plot visualisations were used to identify and remove outliers in the data sets (as detailed in Appendix B in Supplementary Material). Furthermore, the similarity between the data sets of the duplicate reactors was compared using Microsoft Excel Data Analysis two-sample t-tests with a 5% significance threshold.

3. Results

3.1. Pharmaceuticals

For all the studied pharmaceuticals, the concentrations in the produced concentrate were lower than in the spiked reject water feed (Fig. 2A). This was contrary to NH_4-N that was up-concentrated ca. 13 times from 977 ± 43 mg L^{-1} in the feed to 12.7 ± 0.8 g L^{-1} in the concentrate. Erythromycin exhibited the lowest concentration (0.02 ± 0.00 µg L^{-1}) in the concentrate, followed by diclofenac (0.11 ± 0.03 µg L^{-1}) and carbamazepine (0.26 ± 0.06 µg L^{-1}). The highest concentrations in the concentrate were observed for ciprofloxacin (2.6 ± 2.1 µg L^{-1}) and metoprolol (3.5 ± 1.3 µg L^{-1}), compared to 6.4 ± 1.1 µg L^{-1} and 17.8 ± 0.7 µg L^{-1}, respectively, in the feed. Ciprofloxacin and metoprolol, however, also showed the largest deviation in the concentrate concentration measurements without displaying any clear outliers (see Appendix B in Supplementary Material) or statistically significant differences between the datasets from the two reactors ($p >> 0.05$). Especially for ciprofloxacin, this deviation could be due to the fluctuating recovery efficiency observed for the SPE (92 ± 63%; Table SB.9).

The pharmaceutical concentrations measured in the concentrate translated into negligible fractions of the total pharmaceutical mass balances due to the concentrate production rate being only 3.4 ± 0.8% of the feed rate. The highest percentual fractions (1.4 ± 1.1% for both) in the liquid concentrate were observed for ciprofloxacin and metoprolol (Fig. 3). For the other three compounds, only ≤ 0.1% of the input amount was detected in the liquid concentrate. As previously discussed [10], the closed-circuit run experienced issues with leakage from the concentrate chambers of the duplicate reactors leading to a 38 ± 6.5% loss of NH_4-N (Fig. 3). However, even if a similar loss was considered for pharmaceuticals, the maximum permeation into the liquid concentrate would only increase up to 2.3% for ciprofloxacin and 2.2% for metoprolol, which remain negligible in the total mass balance.

In the control experiments in open circuit (Figure SC.1), no permeation into the concentrate took place. It can therefore be concluded that the electric current was the driving force for permeation (as migration), whereas diffusion played no role for the pharmaceuticals. For NH_4-N in the control experiments, on the other hand, some diffusion from the concentrate chamber to the anode and cathode chambers was observed (negative permeation in Figure SC.1) due to osmotic pressure resulting from the initially higher NH_4-N concentration in the concentrate chamber compared to the rest of the system.

On average 33–88% of all the studied pharmaceuticals were not detected in the three outflows – concentrate, effluent or desorption solution. As no similar loss was observed in the control experiments (Figure SC.1), this fraction was attributed to alteration as a result of the EAOPs taking place at the BDD anode (Fig. 3). The EAOPs were thereby the main removal mechanism for all pharmaceuticals in the studied system, as discussed further in Section 4.1. For diclofenac, adsorption also played an important role (30 ± 1.4% total adsorption, i.e., adsorption in the concentrate chamber and the rest of the system combined), whereas it remained at ≤ 7.0 ± 0.3% for the other compounds.

3.2. PFASs

Similarly to the pharmaceuticals, the permeation of the tested PFASs into the concentrate was notably lower than for the target nutrient NH_4-N (Fig. 2B). Five of the eight PFASs (PFHpA, PFNA, PFDA, PFHxS and PFOS) were not detected in the concentrate at all. The short-chain (C_6) carboxylic acid PFHxA exhibited the highest measured concentration in the concentrate (0.024 ± 0.013 µg L^{-1}) compared to the feed concentration of 0.036 ± 0.002 µg L^{-1}, the highest influent concentration for all the detected PFASs. Another short-chain (C_5) carboxylic acid PFPeA had the second highest concentration of 0.012 ± 0.017 µg L^{-1} in the concentrate despite not being detected in the feed. The PFASs present in the concentrate at the highest concentrations had large standard deviations but no statistical conclusions could be drawn due to the low sample numbers. In general, having not been spiked into the feed, the PFAS concentrations in the feed and their concentrations were notably lower in the ng L^{-1} range compared to the pharmaceuticals.

As detailed in Section 2.7, the fate of the PFASs in the EC-EAOP system was not examined as percentual mass balances but rather by looking into the differences in the PFAS in- and outflows (i.e., feed, concentrate and effluent as visualised in Fig. 1). The highest concentration of PFHxA also translated to the highest mass (1.2 ± 1.0 ng) in the concentrate, but this was only 2.8% of the total output. The even lower masses of PFPeA (0.4 ± 0.6 ng) and PFOA (0.04 ± 0.06 ng) in the concentrate were also ≤ 3% of the total outputs of 13 ± 1.0 and 7.3 ± 6.1 ng, respectively.

At the same time, the sulfonic acid (C_8) PFOS was completely transformed in the EC-EAOP system (Fig. 4). Another sulfonic acid (C_6) PFHxS as well as the long-chain (C_8–C_9) carboxylic acids PFOA and PFNA were also partly altered, with the effluent masses being on average 27–81% lower than the inputs. Conversely, the amounts of the carboxylic acids PFHpA (C_7) and PFDA (C_{10}) increased by ca. 7- and 2.5-fold, respectively, which will be discussed further in Section 4.2. Similarly to the concentrate samples, large deviations were also observed for the effluent samples. However, the two-sample t-test only revealed statistically significant differences ($p = 0.01$) between the effluent datasets for PFOA (marked with an asterisk in Fig. 4).

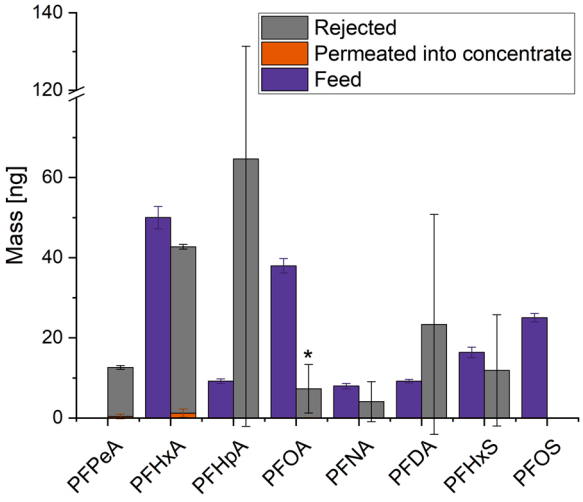

Fig. 4. Comparison of the inflow and outflow masses for the different PFAS compounds during the final 24 h of the closed-circuit experiment. *Statistically significant difference ($p = 0.01$) observed between the effluent data from the two reactors.

4. Discussion

4.1. Pharmaceuticals: permeation and removal

The differences in the permeation of the pharmaceutical compounds into the concentrate chamber can largely be explained by differences in their pH-dependent speciation, which in turn affects their lipo-/hydrophilicity (expressed as log D) (Figs. SA.1 and SA.2). Generally, compounds with an opposite charge to the IEM interact with it (i.e., permeate or adsorb), whereas compounds with the same charge are repulsed. Lipophilicity has been found to increase the adsorption affinity [46] while hydrophilic compounds migrate through the IEMs more easily.

In the applied operational scheme, the pharmaceuticals first entered the cathode chamber with an average pH of 10.1 ± 0.3 in the closed-circuit experiment. Out of the two compounds that permeated into the concentrate the most efficiently (ciprofloxacin and metoprolol), ciprofloxacin was present as a hydrophilic anion at the cathodic pH (Fig. 5A), which suggests it could permeate into the concentrate chamber through the AEM. Diclofenac was also predominantly present as negatively charged but its hydrophilicity was low (Fig. 5A and C). The negligible permeation efficiency (0.08 ± 0.04%) accompanied with the highest adsorption affinity out of all the studied compounds (30 ± 1.4%; Fig. 3) suggests diclofenac was preferentially adsorbed on the positively charged AEM rather than permeating through it, in line with previous observations of diclofenac being among the compounds most prone for adsorption in an electrodialysis stack [46]. The control experiment OC–pH also suggests most of the diclofenac adsorption took place in the cathode chamber (Fig. SC.1).

On the anodic side (at pH 3.6 ± 1.6), both ciprofloxacin and metoprolol were present as hydrophilic cations (Fig. 5B), thus able to permeate the CEM towards the concentrate. Similarly, erythromycin was present at the anode as a clearly hydrophilic cation, but its permeation (0.1 ± 0.1%) was considerably lower than that of ciprofloxacin and metoprolol (1.4 ± 1.1%). A possible explanation is size exclusion: erythromycin has a molecular weight of 733.93 g mol^{-1}, more than double than that of the other studied compounds (Table SA.1).

Carbamazepine, a compound notoriously recalcitrant to wastewater treatment processes including the AD of sewage sludge [51], remained neutral and clearly lipophilic throughout the EC-EAOP system (Fig. 5). This led to negligible permeation (0.06 ± 0.02%) and adsorption (1.4 ± 0.01%). Nevertheless, 56 ± 1.4% of carbamazepine was altered in the system due to the EAOPs (Fig. 3). This shows that BDD-facilitated EAOPs are effective in removing even the most persistent CECs.

In total, the transformation of pharmaceuticals via EAOPs ranged between 33 ± 4.7% for diclofenac and 88 ± 4.3% for ciprofloxacin. As analysing for the potential transformation products originating from the oxidation of the pharmaceuticals was beyond the scope of this study, no definite conclusions about the complete mineralisation of the studied compounds can be drawn. These intermediate by-products can sometimes be even more harmful than the original parent compounds [52, 53], which is why their generation is not desired. For example, the oxidation of diclofenac has been found to lead to the formation of several different aromatic intermediates that consequently have also been associated with increased toxicity levels, causing inhibition of the bacterial strain *Vibrio fischeri* [53]. However, the intermediate(s) responsible for the toxicity could not be implicitly identified. Similarly, ciprofloxacin has been found to transform into different toxic phthalates when subjected to electrochemical peroxidation [52]. Generally, however, BDD electrodes have been reported highly efficient in mineralising CECs, with little intermediate production observed [17].

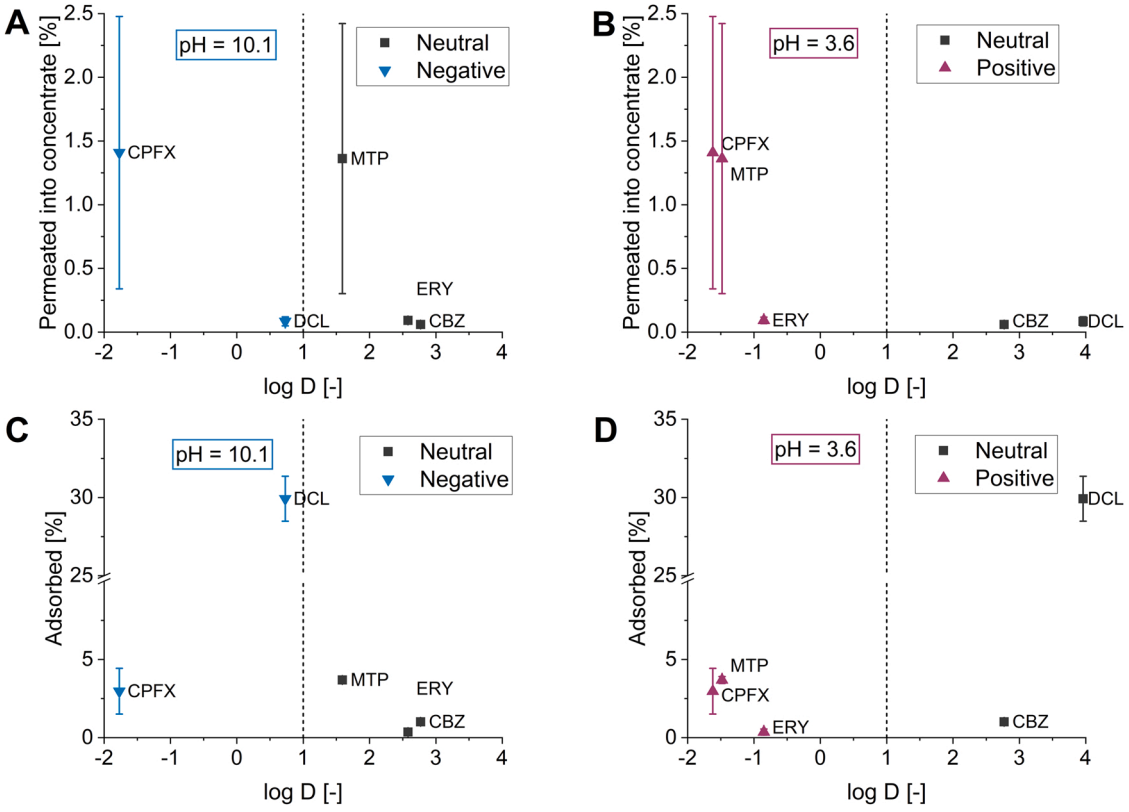

Fig. 5. The permeation into concentrate (A–B) and adsorption (C–D) of different pharmaceutical compounds as a function of their lipophilicity (log D) at the average cathode pH 10.1 (A and C) and average anode pH 3.6 (B and D). The symbol shape and colour indicate the dominating charge of each compound at the corresponding pH. An increase in the log D value means increased lipophilicity, with log D = 1 meaning equal distribution between the octanol and water phases. CBZ = carbamazepine; CPFX = ciprofloxacin; DCL = diclofenac; ERY = erythromycin; MTP = metoprolol.

Given the oxidation efficiency of the BDD electrodes, the incomplete transformation of the pharmaceuticals was most likely due to mass transfer limitations [17]. Furthermore, the hydroxyl radicals generated by the BDDs do not selectively oxidise only the target CECs but all organics [54], and the relatively high organic content of reject water (typically ranging from 442 to 1265 mg L^{-1} for the reject water used in this study [10]) could therefore have affected the pharmaceutical degradation. A more complete organics mineralisation could potentially be achieved using longer HRTs, but the viability of this should be evaluated based on other operational requirements and targets.

Furthermore, the adsorption observed in the closed-circuit run was lower than in the control experiments (Figure SC.1) for all pharmaceuticals studied here, which suggests the EAOPs reduced the adsorption. This trend is favourable because breakthrough of adsorbed CECs through IEMs in longer-term operation has been reported before [46].

4.2. PFASs: permeation and transformations

The short-chain perfluorinated carboxylic acids PFPeA (C_5) and PFHxA (C_6) and the long-chain PFOA (C_8) were the only PFASs observed permeating into the concentrate. The permeation of PFOA (0.04 ± 0.06 ng) was, however, an order of magnitude lower than that of PFPeA (0.4 ± 0.6 ng) and PFHxA (1.2 ± 1.0 ng). The higher permeation tendency of PFPeA and PFHxA is likely due to their smaller size compared to the longer-chain PFASs, with their molar masses being in the same range with most of the studied pharmaceuticals (200–300 g mol^{-1}; Tables SA.1 and SA.2). So far, little experimental data on the physico-chemical properties of different PFASs exists, but modelling approaches have suggested that the shorter-chain PFASs are also more hydrophilic compared to the longer-chain ones with a similar functional group [55]. Furthermore, PFSAs have been estimated to be more lipophilic than PFCAs based on modelling [55], which could explain the lack of PFHxS and PFOS in the concentrate. As acids dissociate in water as anions, the PFASs likely permeated into the concentrate from the cathodic side through the AEM.

In general, the amount of some PFASs decreased in the system while it increased for some (Section 3.2). The observed increase for the short-chain carboxylic acids PFPeA (C_5) and PFHpA (C_7) (Fig. 4) can be explained by the corresponding longer-chain carboxylic acids breaking down to short-chain compounds as a result of the EAOPs [50]. Interestingly, an increase was observed also for the longest-chain compound measured, PFDA (C_{10}) (Fig. 4B). It should, however, be noted that the samples were not analysed for longer-chain PFASs (C > 10). It is therefore possible such larger compounds were present in the reject water and decomposed into PFDA in the EC-EAOP system. Another option is the presence of different PFASs precursors (not analysed) that could have degraded into PFDA under the oxidative conditions [56].

A previous study carried out utilising EAOPs for real secondary wastewater and river water samples reported high oxidation efficiencies of ≥ 95% for long-chain PFCAs (C_8–C_{18}) using a Si/BDD electrode, whereas the removal of short-chain PFCAs (C_3–C_6) was lower in the range 39–70% with the efficiency increasing with increasing chain length [57]. This is in line with the higher transformation efficiency observed for the long-chain PFCAs (on average 50–81% excluding PFDA) and PFSAs (100% for PFOS) compared to the short-chain ones (ca. 17% for PFHxA and 70% for PFHxS, and an increase for the rest) in this study (Fig. 4). It has been suggested that the most likely degradation pathway for PFASs is direct electron transfer with the BDD electrode, whereas the hydroxyl radicals produced by the BDD are inefficient in PFAS oxidation [58,59].

4.3. Applicability of the concentrated nutrient product as a fertiliser

The ultimate goal of the proposed EC-EAOP technology is to produce a nitrogen-rich liquid fertiliser for agricultural use, which means that the amount of CECs in the product should be minimised. A cut-off value of 100 μg kg_{soil}^{-1} has been used for most pharmaceutical compounds (including carbamazepine, diclofenac and erythromycin) in some previous risk assessments on possible contamination through sewage sludge application on farmland in the Nordic countries [41,60]. A lower cut-off value of 10 μg kg_{soil}^{-1} has been applied to compounds exerting detrimental effects at very low concentrations, such as hormones and beta-blockers (including metoprolol) [41,60].

Therefore, when determining the potential release of CECs into the environment, a key parameter of a waste-derived fertiliser product is the ratio of each CEC versus its NH_4-N content (in μg kg_N^{-1}) [61], as the nutrient level of any fertiliser product determines how much of it will be needed on agricultural land. In the concentrate produced here, the pharmaceuticals ciprofloxacin (ca. 208 μg kg_N^{-1}) and metoprolol (ca. 276 μg kg_N^{-1}) displayed the highest concentrations relative to the nitrogen content. For the other three pharmaceuticals, the ratios were order(s) of magnitude lower, ranging from ca. 1.9 μg kg_N^{-1} for erythromycin to ca. 20 μg kg_N^{-1} for carbamazepine in the nutrient product. Similarly, the ratios of the three PFAS compounds permeated into the concentrate were low at ca. 1.0 μg kg_N^{-1} for PFPeA, 1.9 μg kg_N^{-1} for PFHxA, and 0.06 μg kg_N^{-1} for PFOA.

The nitrogen fertiliser application rate depends on many factors, such as the farmland location and characteristics as well as the cultivated crop. Based on the calculations detailed in Appendix E in Supplementary Material, it was concluded that the theoretical maximum metoprolol concentration after one year of fertiliser application using the concentrate produced here would be ca. 0.02 μg kg_{soil}^{-1}. This is notably lower than the 10 μg kg^{-1} considered as the cut-off value for environmental risk posed by metoprolol in soil [41,60]. For the other pharmaceuticals studied here, the final soil concentrations would be even lower and thereby well below the cut-off limits for environmental risk consideration. Similarly, the PFAS concentrations in the soil would be very low at ≤ 0.1 ng kg_{soil}^{-1}. However, more research is needed to determine the cut-off concentrations for environmental risks posed by PFASs in the soil.

As mentioned previously, few studies so far have produced comparable values about the ratio of CECs versus NH_4-N in reject water-derived nutrient products. However, such values can be calculated for the liquid concentrate produced by Arola et al. [14] in an electrodialysis stack from synthetic reject water spiked with CECs at 10 μg L^{-1} based on the concentrations provided by them. Overall, the ratios were higher than obtained in this study, the ratio being slightly higher for diclofenac (ca. 27 μg kg_N^{-1}) and already an order of magnitude higher for carbamazepine (ca. 236 μg kg_N^{-1}) and metoprolol (2 546 μg kg_N^{-1}) [14]. As the CEC concentrations in the concentrate (ranging from 0.1 μg L^{-1} for diclofenac to 9.4 μg L^{-1} for metoprolol) obtained by Arola et al. were similar compared to this study, the higher CECs versus NH_4-N ratios were due to the lower NH_4-N concentration of 3.7 g L^{-1} in the concentrate [14], compared to the 12.7 ± 0.8 g L^{-1} obtained in this study. In dewatered biosolids (which are typically used as fertilisers more often than the liquid reject waters), the ratios of both pharmaceuticals and PFASs to NH_4-N have been reported even higher ranging between ca. 6–18 mg kg_N^{-1} for carbamazepine, ciprofloxacin, diclofenac and metoprolol, and ca. 3 mg kg_N^{-1} for PFASs [41]. Both the NH_4-N and CEC concentrations in digested biosolids naturally vary significantly depending on the origin of the digestate, the AD operational conditions and even the dewatering method [41,62,63]. Generally, however, it can be estimated that the average NH_4-N content of dewatered anaerobically digested sewage sludge is in the 10^0–10^1 mg $kg_{dry\ weight}^{-1}$ range [41,62,63]. At the same time, the pharmaceutical concentrations in these dewatered sludge digestates are often reported in the 10^0–10^2 μg $kg_{dry\ weight}^{-1}$ range [37,40], which translates to CECs to NH_4-N ratios of ca. 10^{-1}–10^1 mg kg_N^{-1}. This suggests that concentrates derived from reject waters could be considered a safer recycled fertiliser than the solid fraction from the CECs point of view.

Nevertheless, the safety and suitability of the generated nutrient product for fertiliser use should be confirmed by cultivation experiments

before adopting it to wider use. Future research should focus on comparing the crop yields obtained with the product obtained here to crops cultivated with commercial fertilisers. The potential generation of toxic intermediates in the oxidation of CECs could also be monitored in toxicity tests, rather than trying to analytically identify all possible transformation products in the product.

5. Conclusions

The fate of five spiked pharmaceuticals and ten indigenous PFASs was studied in a novel EC-EAOP system designed for nitrogen recovery from real reject water. Nitrogen was efficiently up-concentrated from 977 ± 43 mg L^{-1} in the feed to 12.7 ± 0.8 g L^{-1} in the produced liquid concentrate. Metoprolol exhibited the highest pharmaceutical concentration of 3.5 ± 1.3 μg L^{-1} and PFHxA the highest PFAS concentration of 0.024 ± 0.013 μg L^{-1} in the concentrate. Comparison of the organic contaminant concentrations to the NH_4-N concentration in the nutrient product showed that the ratios were low compared to many other waste-derived nutrient products, including dewatered anaerobic digestates. Overall, the pharmaceuticals were altered in the system at average efficiencies of 33–88% via electrochemical advanced oxidation. Sorption of the pharmaceuticals in the system was also carefully monitored but proved to be a relatively unimportant removal mechanism for the studied compounds, except for diclofenac (30 ± 1.4% adsorption). Some PFASs were completely or partly transformed as a result of the EAOPs while the total amount increased for others, especially the short-chain PFPeA and PFHpA, likely as a result of the breakdown of longer-chain PFASs. Future research should be aimed at cultivation tests using the generated nutrient product to both ensure its suitability as a fertiliser and exclude the possible presence of harmful CEC intermediates through toxicity monitoring.

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CRediT authorship contribution statement

Veera Koskue: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Funding acquisition. **Juliette Monetti**: Investigation, Writing – review & editing. **Natascha Rossi**: Investigation, Writing – review & editing. **Ludwika Nieradzik**: Conceptualization, Methodology, Writing – review & editing. **Stefano Freguia**: Conceptualization, Methodology, Supervision, Writing – review & editing. **Marika Kokko**: Conceptualization, Methodology, Supervision, Writing – review & editing. **Pablo Ledezma**: Conceptualization, Methodology, Supervision, Funding acquisition, Writing – review & editing.

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.

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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.2022.107284.

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