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# Use of combined UASB + eMBR treatment for removal of emerging micropollutants and reduction of fouling

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## ABSTRACT

This study employs a novel combined pilot plant consisting of an anaerobic reactor followed by a membrane electrochemical bioreactor (eMBR) to treat domestic water containing selected contaminants of emerging concern (CECs) [ibuprofen (IB), carbamazepine (CBZ), diclofenac (DCF) and 17$\alpha$-ethinylestradiol (EE2)]. The first phase operated as a conventional membrane bioreactor to achieve the removal of organic matter [chemical oxygen demand (COD)], the CECs and phosphorus. A removal rate of 96.3% for COD, 94.5% for IB, 37.1% for CBZ, 87.1% for DCF and 96% for EE2 was obtained. In the three subsequent phases, current density (CD) of 5, 10 and 15 A/m$^2$ was applied successively in the eMBR with the aim of investigating the effects on the removal of the former components and the fouling of the membrane. After the application of 5 and 10 A/m$^2$ CD, the removal rate of COD decreased. Regarding phosphorus, a CD of 5 A/m$^2$ was enough to achieve the rate of 97% and the membrane fouling suffered a substantial reduction too. Finally, the experimental results were subject to statistical analysis using the Kruskal–Wallis and Wilcoxon tests to validate the influence of each CD.

**Key words:** combined treatment, current density effect, membrane fouling, phosphorus removal, UASB + eMBR

## HIGHLIGHTS

- Novel combination of UASB + eMBR technologies proves effective in wastewater treatment.
- UASB stands in COD removal, MBR in CECs removal and eMBR in TP removal.
- A current density of 5 A/m$^2$ is the most efficient in reducing membrane fouling.
- A current density of 5 A/m$^2$ improves the removal of some CECs.

## 1. INTRODUCTION

The fast-paced development of countries inevitably leads to an augmented production and consumption of new synthetic chemical compounds, especially in the field of pharmaceuticals. Consequently, a large number of drugs, metabolites and transformation products – including organic contaminants of emerging concern (CECs) end up in the sewage. This leads to major deteriorating effects on the environment, which is unable to cope with high amounts of contaminants (Rivera-Utrilla *et al.* 2013; Pal *et al.* 2014; Dulio *et al.* 2018; Peña-Guzmán *et al.* 2019).

A large number of processes for wastewater treatment have proved to efficiently remove CECs (Bolong *et al.* 2009; Rivera-Utrilla *et al.* 2013; Ahmed *et al.* 2017). However, CECs are of wide diversity, structure and properties (Stefanakis & Becker 2016; Dulio *et al.* 2018), making necessary the use of coupled treatment technologies to achieve wide-ranging removals (Ahmed *et al.* 2017; Rodriguez-Narvaez *et al.* 2017). For example, urban wastewater treatment processes as the submerged membrane bioreactor (MBR) combines aerobic degradation with membrane filtration. MBRs reduce CECs in wastewater more effectively than the aerobic treatment alone, as it has been previously reported for conventional activated sludge (CAS) treatment systems (Bernhard *et al.* 2006; Kruglova *et al.* 2016; Besha *et al.* 2017).

Regarding anaerobic systems, Harb *et al.* (2019) reported that processes including MBRs and up-flow anaerobic sludge blanket (UASB) reactors can better remove persistent pollutants than aerobic processes, when reviewing the fate of diverse micro-pollutants. Alvarino *et al.* (2014) studied the combination of both a UASB system with a CAS reactor, showing its

effectiveness for the elimination of a selected group of CECs. As the MBR process is more efficient than the CAS process, it is reasonable to think that the combination of a UASB and MBR will allow to achieve excellent effluent quality and higher removals for the CECs (Alvarino *et al.* 2016; Moya-Llamas *et al.* 2018). This combination also seems to be more environmentally sustainable than the solely aerobic treatments, because of energy savings and reduction in sludge production (Lettinga 1995; Chernicharo *et al.* 2015; De La Rubia *et al.* 2019).

Recently, the coupling of aerobic/anaerobic MBRs with an electrocoagulation (EC) unit is being tested (Al-Qodah *et al.* 2019; Ensano *et al.* 2019; Asif *et al.* 2020). The EC unit is located inside the bioreactor, configuring an electrochemical membrane bioreactor (eMBR). The electric currents applied to the electrodes trigger a series of physical and chemical processes. For example, when using aluminum anodes, $OH^-$ anions are simultaneously formed in the cathode releasing hydrogen gas via the electro-reduction of water. Aluminum cations rapidly form insoluble oxyhydroxides and hydroxides, which easily precipitate and form flocs. The flocs formed can either settle, get enmeshed with the activated sludge or get dragged to the surface by the hydrogen microbubbles formed at the cathode (electroflotation). Hence, several mechanisms are documented to promote the pollutant removals – physical processes (coagulation of colloidal or poorly soluble species), adsorption of pollutants in the large Al–O–Al–OH compounds and chemical processes as electro-oxidation of contaminants on the electrodes.

The use of an eMBR has resulted in a reduction of membrane fouling and an overall enhancement of the phosphorus removal from the effluent along with certain CECs such as Diclofenac (DCF), carbamazepine (CBZ) and amoxicillin removals (Ensano *et al.* 2019).

Grouping a UASB reactor with an MBR and an EC unit for treating urban wastewater maybe then of great interest for an improved organic matter, nutrient and CECs removal. To the author's knowledge, no previous published studies have been found that can address such a combination (UASB + eMBR). Therefore, in this work, a UASB + eMBR pilot reactor is approached to evaluate the removal efficiency of four selected CECs, ibuprofen (IB), carbamazepine (CBZ), Diclofenac (DCF) and 17$\alpha$-ethinylestradiol (EE2), pharmaceuticals typically present in urban wastewater. The influence of applying different electric currents, measured as current density (CD), on the removal of organic matter (chemical oxygen demand, COD), CECs, total phosphorus (TP) and the fouling of the membrane was investigated (Figure 1).

## 2. MATERIALS AND METHODS

All the experimentation was carried out in the laboratories of the Institute of Water and Environmental Sciences of the University of Alicante, Spain.

### 2.1. Pilot plant UASB + eMBR

The UASB and MBR pilot reactors used were described in a previous article. The UASB reactor consisted of a vertical cylindrical PVC with an available volume of 25 L which was fed with 8 L of granulated sludge from an industrial wastewater treatment plant for the beer-brewing industry (Quart de Poblet, Valencia, Spain). The device was equipped with a peristaltic

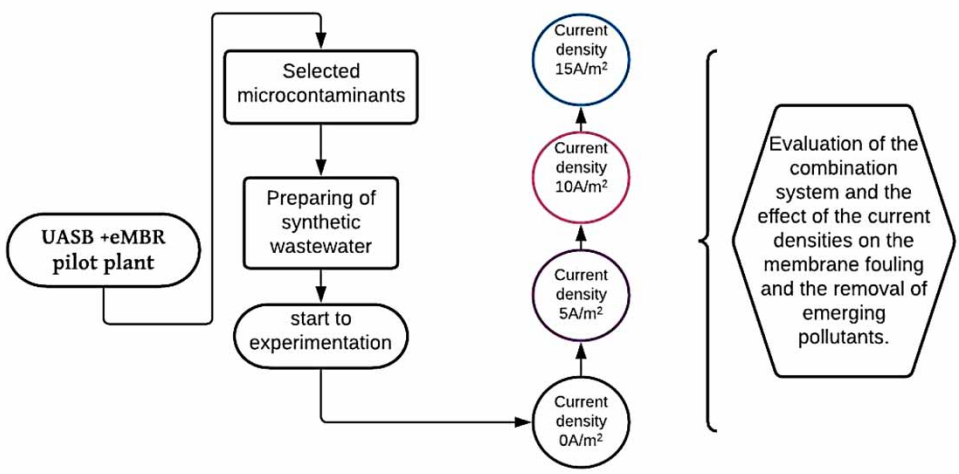



**Figure 1** | Experimentation structure.

recirculation pump (Dosiper, León, Spain) to control and maintain the velocity of the amount of upflowing liquid within the reactor. The MBR, also made of PVC, consisted of an aerobic chamber with an available volume of 18 L, which was fed with 6 L of mixed liquor of activated sludge from a municipal wastewater treatment plant (Rincón de León, Alicante, Spain). The reactor further had a hollow fiber membrane module (Koch brand PURON®) of polyvinylidene fluoride incorporated with an ultrafiltration pore diameter of 0.03 μm and a total filtration area of 0.5 $m^2$. An EC device was incorporated consisting of two concentric cylindrical electrodes built of a perforated metal plate (aluminum anode and stainless-steel cathode), with a separation of 5 cm between them, connected to a direct current generator.

The system was equipped with a temperature measuring device and a sensor to measure the levels of the anaerobic and aerobic reactors. The MBR was equipped with a dissolved oxygen meter (Oxymax COS61 Endress + Hauser) and a pressure transmitter (TPR-14 from DESIN Instruments) to monitor transmembrane pressure (TMP) data. Peristaltic pumps Dosiper C1 R (León, Spain) were used to feed the plant and carry out the recirculation of sludge. The permeate was extracted from the membrane chamber using a Watson-Marlow 323 U/D peristaltic pump (Watson-Marlow Ltd, Falmouth, UK). The critical flux of the membrane was determined with the flow path method developed by van der Marel *et al.* (2009). The software developed by the research group was used for continuous monitoring and control of the main operating parameters of the combined system.

A diagram of the pilot plant is shown in Figure 2.

### 2.2. Operation parameters

The combined system was operated for 103 consecutive days with the parameters indicated in Table 1.

The eMBR reactor was operated consecutively in four phases with four different CD values. During phase 1, the CD was 0 $A/m^2$, that is, the operation was equivalent to a conventional MBR system without EC. In phases 2, 3 and 4, the CD was 5,

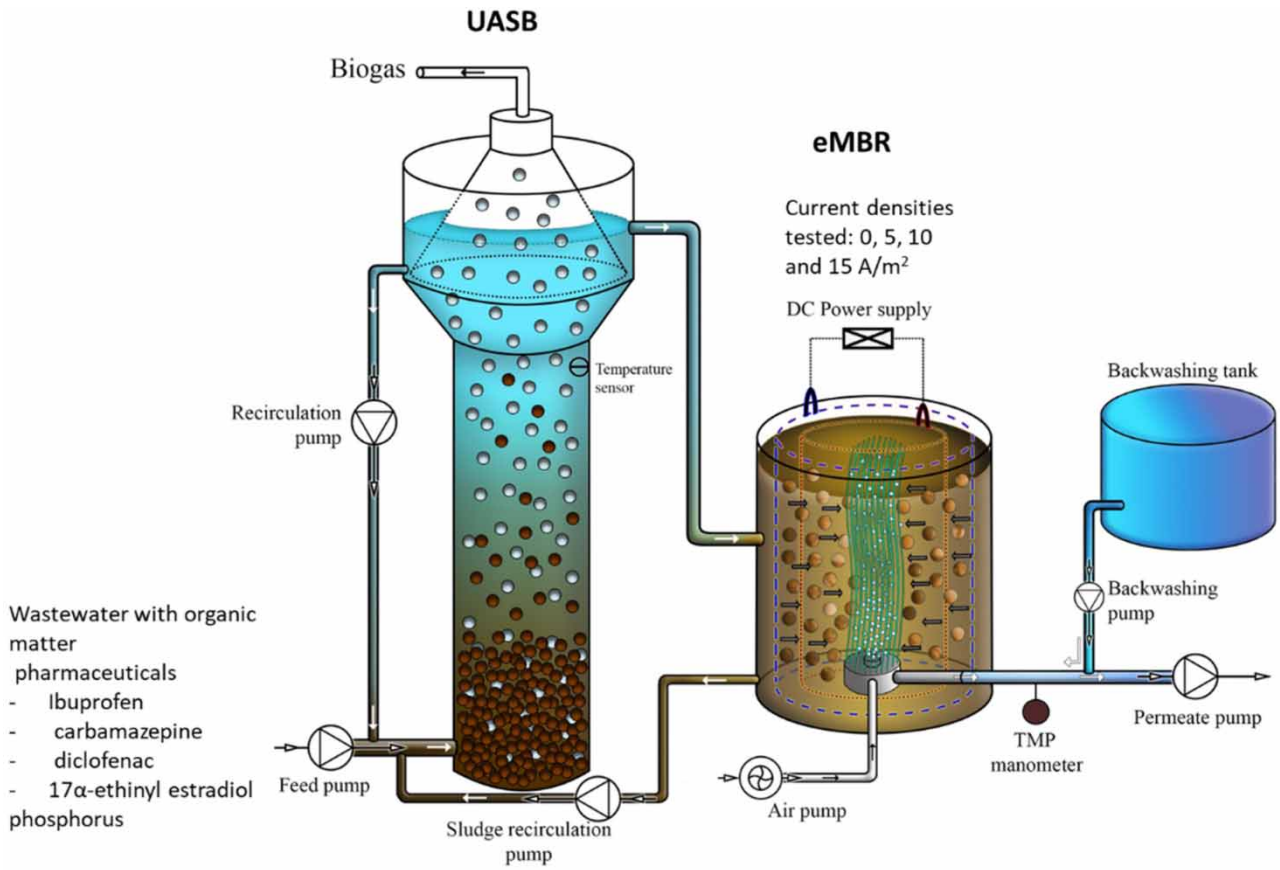



**Figure 2** | Scheme of combined pilot plant UASB + eMBR.

**Table 1** | Operation parameters of the combined system

| Parameter | Unit | Value |
|---|---|---|
| Available volume UASB | L | 25 |
| Available volume eMBR | L | 18 |
| Influent and effluent flow | L/hour | 2 |
| Hydraulic residence time at UASB | hour | 12.5 |
| Hydraulic residence time at eMBR | Hour | 9 |
| Sludge retention time at UASB | Day | 30 |
| Sludge retention time eMBR | Day | >90 |
| Wastewater temperature at UASB | °C | 30 ± 0.3 |
| Operation time/Backwash in eMBR | Minute | 10/1 |
| Time sequence of operation for electrocoagulation | Minute | 5 ON/10 OFF |

10 and 15 A/m$^2$, respectively. At the beginning of phases 3 and 4, a change was made of the activated sludge of the eMBR in order to avoid the initial presence of aluminum in the sludge.

### 2.3. Synthetic wastewater

Urban wastewater of medium-high concentration was simulated, applying the DIN 38412-L24 standard, from casein peptone, extract of meat and urea, and $MgSO_4{\cdot}7H_2O$, $KH_2PO_4$, $CaCl_2{\cdot}2H_2O$ and NaCl.

The synthetic feed was prepared in batches of 200 L (about 3 batches each week) which were stored in a tank, from where it was fed to the UASB reactor. The real average concentration of CO and TP for each of the phases is shown in Table 2.

### 2.4. Selected microcontaminants

Four pharmaceutical drugs were selected, all of them frequently present in urban wastewater: ibuprofen (IB), carbamazepine (CBZ), diclofenac (DCF) and 17$\alpha$-ethinyl estradiol (EE2). The characteristics, main uses, environmental relevance and behavior in CAS and MBR biological treatments are summarized in Table 3.

The four selected pharmaceutical drugs are of great interest to the scientific community due to their widespread consumption and their impact on the environment. The IB is considered a key element by the WHO. It is eliminated in a high percentage in biological treatments, but it maintains a high environmental presence due to its large production and consumption, which is over 25,000 tons worldwide (Ma *et al.* 2018). CBZ and DCF are especially resistant in different treatment systems and conditions. In fact, CBZ, due to its persistence to treatments, was proposed as a marker to detect anthropogenic influence in the aquatic environment (Clara *et al.* 2003). Switzerland, the first country in the world to impose the control of CECs in wastewater treatment plants (Bui *et al.* 2016), includes these two pollutants in a reduced list of standardized monitoring micro-pollutants for which 80% removal must be achieved in treatment plants (Eggen *et al.* 2014). Additionally, the DCF is of great interest to the entire EU, since it was included, together with EE2, in the first watch list (Comisión Europea 2015). EE2 is undoubtedly a substance of great environmental concern, as it is currently included in the EU's watch and monitoring list (Comisión Europea 2018).

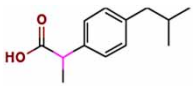
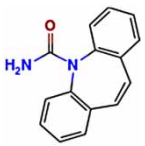
The concentration of each drug in synthetic wastewater was established at 10–25 μg/L, which is an environmentally significant range at which these compounds can be found in wastewater and do not influence the microbial activity of biological processes, according to toxicity tests carried out in previous investigations by our group (Moya-Llamas *et al.* 2019).

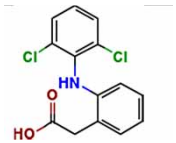
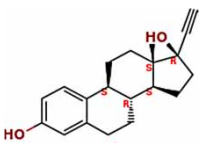
**Table 2** | Actual mean concentration of COD and TP for each of the phases

| Parameter | Phase 1 (0 A/m$^2$) | Phase 2 (5 A/m$^2$) | Phase 3 (10 A/m$^2$) | Phase 4 (15 A/m$^2$) |
|---|---|---|---|---|
| COD affluent to the UASB (mg/L) | 737.2 ± 66.4[a] | 716.0 ± 92.1 | 751.9 ± 89.8 | 834.5 ± 68.5 |
| TP affluent to the eMBR (mg/L) | 24.2 ± 2.6 | 22.8 ± 2.3 | 22.8 ± 0.1 | 21.8 ± 0.1 |

[a]Average ± standard deviation.

**Table 3** | Selected pharmaceutical microcontaminants

| Compound<br>CAS no.<br>Molecular formula<br>Structure[a]<br>Henry's law constant ($K_H$) at 25 °C (atm $m^3$/mol)<br>Log Kow (octanol–water partition coefficient)[b] | Uses | Environmental relevance[c] | Behavior in CAS and MBR biological treatments |
|---|---|---|---|
| Ibuprofen<br>15687-27-1<br>$C_{13}H_{18}O_2$<br>  <br>$1.5 \times 10^{-7}$<br>3.97 | Antipyretic, analgesic and anti-inflammatory | According to the classification provided by companies to ECHA in REACH registrations, this substance is harmful if swallowed, causes serious eye irritation, may cause respiratory irritation and causes skin irritation. Significant environmental risk in coastal sediments (Pusceddu *et al.* 2018) and effects on fish (Islas-Flores *et al.* 2014; Gutiérrez-Noya *et al.* 2020) | Removal CAS treatments >90% (Nakada *et al.* 2006) and 90–97% in MBR (Tadkaew *et al.* 2011) |
| Carbamazepin<br>298-46-4 $C_{15}H_{12}N_2O$<br>  <br>$1.08 \times 10^{-7}$<br>2.45 | Analgesic, antiepileptic and treatment of other nervous disorders | According to the classification provided by companies to ECHA this substance is harmful if swallowed, is suspected of damaging fertility or the unborn child, may cause harm to breast-fed children, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing difficulties if inhaled. At concentrations in wastewater, it presents potential risks for bacteria, algae, invertebrates and fish (Ferrari *et al.* 2003) | Removal in CAS treatments <50% (Nakada *et al.* 2006) and 0–96% in MBR (Krzeminski *et al.* 2019) |

| | | | |
|---|---|---|---|
| Diclofenac<br>15307-86-5<br>$C_{14}H_{11}Cl_2NO_2$<br>  <br>$4.73 \times 10^{-12}$<br>4.51 | Analgesic, anti-inflammatory | According to the classification provided by companies to ECHA in REACH registrations this substance causes damage to organs through prolonged or repeated exposure, is toxic to aquatic life with long-lasting effects, is harmful if swallowed and is suspected of damaging fertility or the unborn child. It is the compound with the highest acute toxicity of the non-steroidal anti-inflammatory drugs and can exert effects of chronic and acute toxicity on the liver, kidneys and gills of fish (Ferrari *et al.* 2003; Vieno & Sillanpää 2014) | Removal in CAS treatments 0–81% and 0–87% in MBR (Krzeminski *et al.* 2019) |
| 17$\alpha$-Ethinylestradiol<br>57-63-6<br>$C_{20}H_{24}O_2$<br>  <br>$7.94 \times 10^{-12}$<br>3.67 | Synthetic estrogen, contraceptive, breast cancer treatment | According to the classification provided by companies to ECHA this substance may cause cancer, may damage fertility or the unborn child, is very toxic to aquatic life with long lasting effects, causes damage to organs through prolonged or repeated exposure, and may cause harm to breast-fed children. It is included in the list of EU observation (Comisión Europea 2018) | Removal in CAS treatments 18–94% range and 20–100% in MBR (Krzeminski *et al.* 2019) |

[a]http://www.chemexper.com/.

[b]PubChem substance and compound databases.

chttps://echa.europa.eu/es/information-on-chemicals/registered-substances, and other references.

### 2.5. Controlled parameters and sampling frequencies

Table 4 indicates the parameters analyzed and the sampling points in each of the phases. The sampling frequency was three times per week in all cases.

### 2.6. Analytical methodology

pH and K were measured using a CRISON (CM35) pH/conductivity meter. T was measured using a turbidimeter (TBI Velp Scientifica). MLSS and MLVSS contents were based on gravimetric Standard Methods (APHA 1998). F was measured using an Albet 400 filter. $\mu$ was measured using a Smart Series L Model Rotational Viscometer. COD, $NO^{3-}$, $NO^{2-}$, $NH^{4+}$, TN and TP analyses were performed based on colorimetric methods (tube-test Spectroquant® and spectrophotometer NOVA 60 Machery-Nagel GMBh).

The soluble and bound EPS were calculated by summing proteins, carbohydrates and humic acids, applying a method optimized by our group (Domínguez Chabaliná *et al.* 2013). EPS extraction was carried out by ion exchange using a cation resin (Frolund *et al.* 1996). A total protein kit (Sigma-Aldrich, TP 0330) was used for protein determination, according to the method of Lowry *et al.* (1951). Carbohydrates are determined through the phenol-sulfuric acid colorimetric method reported by Dubois *et al.* (1956). The determination of humic acids was carried out using the colorimetric method of Frolund *et al.* (1996).

The quantification and analysis of the drugs were based on the methodology proposed by De Almeida Azevedo *et al.* (2000). Samples were taken in sterilized bottles, separating the suspended solids with 1.2 μm fiberglass filters. Solid-phase extraction was performed with a Dionex Auto Trace 280 equipment (Thermo Scientific), using Oasis HLB 6 cc/200 mg cartridges, and the solvents ethyl acetate, methanol and water from Sigma-Aldrich (Steinheim, Germany). The collected extract was dried under N2 flow and reconstituted with 100 μL of internal standard solution (500 μg/L of CBZ d-10 in methanol) and a derivatization reagent (50 μL of BSTFA: TMCS and 50 μL pyridine). The samples were analyzed by gas chromatography coupled to mass spectrometry (GC/MS), using an Agilent 7890 model chromatograph and an Agilent 5975 model quadrupole mass spectrometer.

### 2.7. Statistical analysis

To determine whether the differences observed after applying the different CDs used during EC were statistically significant, the non-parametric tests of Kruskal & Wallis (1952) and Wilcoxon (1992) were applied. A significance value >95% was

**Table 4** | Parameters analyzed and sampling points in each of the phases

| Parameter | Phases | Influent | Effluent UASB | Mix liquor | Effluent eMBR |
|---|---|---|---|---|---|
| pH | All | x | x | x | x |
| Conductivity ($K$) | All | x | x | x | x |
| Turbidity ($T$) | All | x | | | x |
| Redox potential ($E$) | All | x | x | x | x |
| Mixed liquor suspended solids (MLSS) | All | | | x | |
| Mixed liquor volatile suspended solids (MLVSS) | All | | | x | |
| Filterability ($F$) | All | | | x | |
| Viscosity ($\mu$) | All | | | x | |
| Chemical oxygen demand (COD) | All | x | x | | x |
| Nitrate ($NO^{3-}$) | All | x | | | x |
| Nitrite ($NO^{2-}$) | All | x | | | x |
| Ammonium ($NH^{4+}$) | All | x | x | | x |
| Total nitrogen (TN) | All | x | | | x |
| Total phosphorus (TP) | All | | x | | x |
| Extracellular polymeric substances (EPS) | All | | | x | |
| Pharmaceuticals microcontaminants | 1 | x | x | | x |
| | 2,3,4 | | x | | x |

considered, that is, $p < 0.05$. The Kruskal–Wallis test allowed evaluating statistically significant differences in the entire set of experimental results, and the Wilcoxon test allowed comparing each pair of CD combinations.

## 3. RESULTS AND DISCUSSION

### 3.1. Removal of organic matter

Table 5 shows the average percentages of COD removal in each reactor for each phase of the experimentation, and what is the contribution of the eMBR to the elimination of COD that enters the combined system.

The overall average COD removal was very high in all experimental phases, 94–98%, which confirmed that the combination UASB + MBR/eMBR is effective to achieve very high percentages of organic matter removal. The UASB reactor was the largest contributor, removing 75–85% of the initial COD. This excellent performance of the anaerobic reactor operating at OLR of 1.4–1.6 kg COD/$m^3$ d was inconsistent with previous studies by our group (Moya Llamas 2018) and other authors (Alvarino *et al.* 2016). Biogas production was 0.35–0.45 $m^3$ biogas/kgDQO. These results confirm that the UASB reactor could be an excellent choice for the initial degradation of a very high percentage of organic matter from urban wastewater in areas with moderate to warm climates. Energy consumption was lower than with aerobic reactors, less sludge was generated and, in addition, biogas was produced that could be used for energy. In the eMBR reactor, which operates at OLR values of 0.32–0.45 kg COD/$m^3$ d, the average COD removals were also high, 61–91%, although their contribution to the removal of the initial COD was much lower, 9–22%.

The influence of the different CDs on the removal of COD was variable. Average yields compared to conventional MBR decreased with 5 and 10 A/$m^2$ and increased with 15 A/$m^2$. One possible explanation would be that EC modified the characteristics of the biomass and caused two opposite effects: on the one hand, there was a reduction in the fouling of the membrane (Section 3.4), which decreased its ability to filter colloids and reduced the efficiency of removal of COD by filtration; on the other hand, when the CD increased, the influence of the EC mechanisms and the direct and indirect oxidation of organic matter also increased, and therefore increased the efficiency of COD removal within the reactor. For CD of 5 and 10 A/$m^2$, the filterability effect prevailed, while at 15 A$m^2$, the greater removal offset the effect of the greater filterability (Borea *et al.* 2017; Mendes Predolin *et al.* 2021).

### 3.2. Micro-pollutants removal

The elimination of organic micro-pollutants in water treatment plants depends on their physical–chemical properties, the type of treatment, the operating conditions and the environmental conditions (Virkutyte *et al.* n.d.). Possible mechanisms to consider are volatilization, direct and indirect photodegradation, sorption and biodegradation. The volatilization of organic solutes from the water surface is associated with Henry's law constant ($K_H$). The low $K_H$ values for the pollutants investigated (Table 3) allow qualifying these compounds as essentially non-volatile (Lyman *et al.* 1990). Therefore, the contribution of the volatilization mechanism to removal is negligible. Photodegradation can also be considered negligible due to the small surface exposed to radiation in our experimental device (Figure 2). Sorption in sludge is related to the ethanol–water partition coefficient Kow. The Log Kow values are between 2.45 and 4.51 (Table 3), so it can be considered a medium sorption potential (Rogers 1996). This sorption is essential for biodegradation to take place in the active biomass of the sludge, but it can also lead to part of the pollutants being eliminated with the excess sludge in the purification processes. Sorption of these compounds was investigated in a previous work with UASB and MBR reactors (Bernal-Romero del Hombre Bueno *et al.* 2018), and only for EE2, a small percentage of 0.4% was found in the excess sludge from the UASB reactor. Consequently,

**Table 5** | Average percentages of COD removal in each reactor and contribution of the eMBR to the removal of the initial COD

| Phase | COD in UASB effluent (mg/L) | COD removal in UASB (%) | COD in final effluent (mg/L) | COD removal in eMBR (%) | eMBR contribution to the removal of the initial COD (%) | COD total removal (%) |
|---|---|---|---|---|---|---|
| 0 (0 A/$m^2$) | 168.5 ± 65.1 | 76.7 ± 7.7 | 25.8 ± 18.9 | 84.2 ± 10.2 | 19.6 ± 7.6 | 96.3 ± 2.8 |
| 1 (5 A/$m^2$) | 120.5 ± 60.1 | 84.4 ± 6.3 | 45.3 ± 22.9 | 61.2 ± 25.4 | 9.4 ± 6.8 | 93.8 ± 3.4 |
| 2 (10 A/$m^2$) | 119.0 ± 25.9 | 85.2 ± 4.7 | 24.3 ± 18.5 | 78.0 ± 18.4 | 11.8 ± 5.1 | 97.0 ± 2.0 |
| 3 (15 A/$m^2$) | 162.3 ± 66.2 | 75.8 ± 16.7 | 18.7 ± 20.0 | 90.8 ± 6.7 | 22.0 ± 15.3 | 98.0 ± 2.6 |

Average ± standard deviation.

it can be affirmed that the removal of the four micro-pollutants in our experimental device was produced mainly by biodegradation. Biodegradation is highly conditioned by the molecular structure. Tadkaew *et al.* (2011) studied the effect of the presence of electron donor or subtractor groups: compounds containing strong electron-donating functional groups show high biodegradation, such as EE2 containing the hydroxyl group −OH; compounds containing strong electron-withdrawing groups show low biodegradation, such as CBZ containing an amide group −CONR2; Compounds with electron donors and acceptors show variable behaviors, such as IBF, which contains the hydroxyl group −COOH (donor) and the methyl group −CH3 (acceptor) and DCF, which contains the amine group −NHR1R2 (donor) and the groups −COOH and −Cl (acceptors).

### 3.2.1. Phase 1 (CD = 0 A/m$^2$)

Table 6 shows the average inlet and outlet concentrations of each pollutant to each reactor, the average removal percentage in each reactor, and the contribution of the MBR to the global removal of each micro-pollutant.

The removal percentages in the UASB reactor were relatively low: IB 24.1%, CBZ 23.2%, DCF 29.0% and EE2 26.5%, in accordance with the literature (Reyes-Contreras *et al.* 2011; Queiroz *et al.* 2012; Brandt *et al.* 2013; Alvarino *et al.* 2014, 2016). An interesting fact when looking at a previous analysis by our group (Moya Llamas 2018) is that removals were observed in the UASB reactor of 20–61% for DCF and 70–90% for EE2. The lowest percentages corresponded to the highest organic loading rate (OLR) tested (0.67 kg COD/m$^3$). In the present investigation, the ORL was even higher, 1.4–1.6 kg DOC/m$^3$ d, which might explain the low removal values of DCF and EE2 found. Similar behavior has been reported for other CECs in anaerobic reactors (Carneiro *et al.* 2020).

The mean removal percentages in the MBR were 94.3% for IB, 18.2% for CBZ, 86.0% for DCF and 95.8% for EE2. The least degraded compound was CBZ, due to its stable heterocyclic structure, presence of the strongly electron-accepting amide group, and hydrophilic nature (Log Kow = 2.45) (Reif *et al.* 2008; Tadkaew *et al.* 2011; Asif *et al.* 2019; Tiwari *et al.* 2019). DCF achieved high removal, although it has been considered by many authors as a recalcitrant compound due to its low lipophilicity and poorly biodegradable nature. However, other authors report relatively high removal rates: Radjenović *et al.* (2009) obtain 65%, Vieno & Sillanpää (2014) report 23–85, Moya-Llamas *et al.* (2018) obtain 30–75%. In our investigation, the average removal of DCF reached 86%, which might be due to the elevated age of the sludge (SRT) being over 90 days, which allowed the bacterial population to be more diversified and to be able to degrade DCF, either by direct metabolism or by co-metabolic degradation through enzymatic reactions (Vieno & Sillanpää 2014; Hai *et al.* 2015). Consistent with this rationale, Asif *et al.* (2019) report removals for DCF of 50% for SRT of 30 days, and of more than 90% for SRT of 80 days. It should also be considered that DCF is much more lipophilic (log Kow = 4.35) than CBZ, which will allow its greater sorption in the sludge resulting in a facilitated biodegradation.

Figure 3 shows the average contribution of each reactor of the combined system of the removal of the CECs entering the system. The reactor that contributes the most is the MBR, except for CBZ.

Suarez *et al.* (2010) studied the behavior of these micro-pollutants under nitrifying and denitrifying conditions, considering very long adaptation times of the biomass, and classified them according to their aerobic and anoxic biodegradability: the BI was highly biodegradable under aerobic and anoxic conditions, the CBZ resistant to biological transformation, and DCF and EE2 highly biodegradable under aerobic conditions but persistent under anaerobic conditions. Our results can confirm this behavior, except for the IB that showed low removal under anaerobic conditions. The overall mean removal percentages in the combined system were 94.5% for IB, 37.1% for CBZ, 87.1% for DCF and 96.0% for EE2.

**Table 6** | Average concentrations and average removal percentages for each micro-pollutant during phase 1 (CD = 0 A/m$^2$)

| Micro-pollutant | Affluent (μg/L) | UASB effluent (μg/L) | UASB removal (%) | Final effluent (μg/L) | MBR removal (%) | MBR contribution to global removal (%) | Total removal (%) |
|---|---|---|---|---|---|---|---|
| IB | 9.2 ± 2.8[a] | 7.0 ± 1.3 | 24.1 ± 17.9 | 0.5 ± 0.2 | 92.7 ± 3.2 | 70.4 ± 18.2 | 94.5 ± 2.8 |
| CBZ | 22.9 ± 1.8 | 17.6 ± 5.3 | 23.2 ± 13.5 | 14.4 ± 2.7 | 18.1 ± 8.3 | 13.9 ± 17.6 | 37.1 ± 11.5 |
| DCF | 19.7 ± 3.7 | 14.0 ± 1.4 | 29.0 ± 14.0 | 2.5 ± 1.1 | 82.0 ± 8.1 | 58.2 ± 14.5 | 87.1 ± 4.9 |
| EE2 | 11.6 ± 2.0 | 8.5 ± 1.0 | 26.5 ± 13.6 | 0.5 ± 0.1 | 94.6 ± 2.2 | 69.5 ± 24.6 | 96.0 ± 1.7 |

[a]Average ± standard deviation.

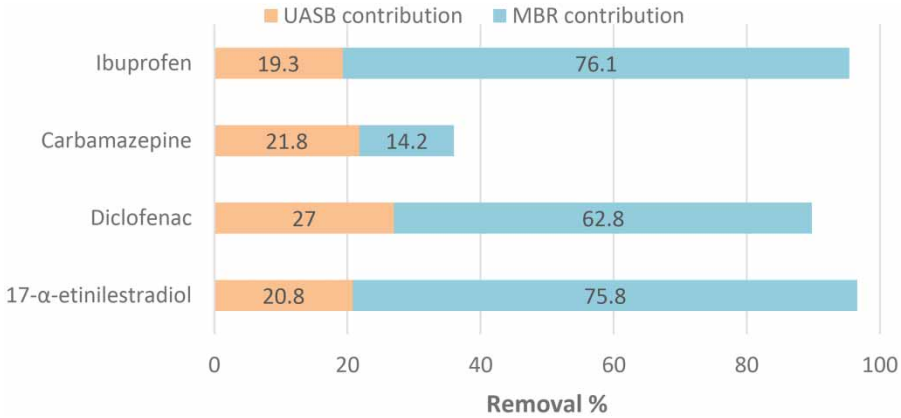



**Figure 3** | Average contribution of each reactor to the removal of CECs entering the system.

### 3.2.2. Phases 2, 3 and 4: effect of CD on micro-pollutant removal

Table 7 shows the average inlet and outlet concentrations of micro-pollutants from the eMBR in each of phases 2, 3 and 4, and the removal percentages achieved. Figure 4 represents the average removal percentage in each of the phases.

When the CD applied for the EC is increased, it causes an increase in the intensity of the associated phenomena: the speed of solubilization of aluminum at the anode, the rate of generation of hydrogen bubbles at the cathode, floc formation and mass transfer at the electrodes (Holt *et al.* 2005; Kabdaşlı *et al.* 2012). The effect on the removal of micro-pollutants can be variable. On the one hand, the increase in CD can increase removal due to the mechanisms of EC, direct anodic oxidation and indirect oxidation by reactive oxygen species generated by the application of the electric field complementing the biological process (Tafti *et al.* 2015; Asif *et al.* 2020; Mollah *et al.* n.d.). On the other hand, the increase in CD can also decrease removal due to the electroflotation mechanism, which occurs when low-dense flocs are dragged to the surface due to the small hydrogen bubbles generated (Chen 2004; Cañizares *et al.* 2007). If this occurs, the micro-pollutants adsorbed on the flocs remain in less appropriate conditions for degradation as they do not interact with the active biomass; Furthermore, this effect shortens the time in which the flocculated matter remains in the effective region of the reactor and reduces the possibility of mixing and adsorbing pollutants and, consequently, decreases the effective use of the coagulant (Bayar *et al.* 2011). Electroflotation mechanism will favor CDs high because the speed is increasing the production of bubbles. As a consequence of the fact that an increase in CD implies the intensification of mechanisms that increase or decrease removal, it is possible that for each specific pollutant, there may be an optimal range of CD that improves removal in eMBRs.

Table 7 and Figure 4 show that in the case of IB, its removal was not favored for any CD value. When applying the Wilcoxon statistical analysis to the experimental results, significant differences ($p$-value $<0.05$) were found between the results

**Table 7** | Average inlet and outlet concentrations of the eMBR reactor in each of phases 2, 3 and 4 and removal percentages achieved

| Microcontaminant | Current density (A/m$^2$) | UASB effluent (μg/L) | Final effluent (μg/L) | eMBR removal (%) |
|---|---|---|---|---|
| Ibuprofen | 5 | 7.5 ± 3.1 | 0.5 ± 0.1 | 92.8 ± 2.3 |
| | 10 | 9.2 ± 1.3 | 1.6 ± 1.0 | 82.9 ± 10.5 |
| | 15 | 12.4 ± 4.6 | 1.7 ± 1.0 | 86.6 ± 5.5 |
| Carbamazepine | 5 | 11.7 ± 2.5 | 8.8 ± 1.6 | 25.0 ± 9.6 |
| | 10 | 26.2 ± 4.4 | 17.6 ± 6.4 | 32.7 ± 22.6 |
| | 15 | 17.8 ± 6.7 | 14.0 ± 9.1 | 21.2 ± 22.5 |
| Diclofenac | 5 | 25.8 ± 16.1 | 2.7 ± 1.8 | 89.7 ± 4.0 |
| | 10 | 13.3 ± 7.7 | 0.6 ± 0.3 | 95.3 ± 4.4 |
| | 15 | 20.9 ± 5.5 | 3.9 ± 3.2 | 81.4 ± 10.6 |
| 17$\alpha$-ethinyl estradiol | 5 | 9.1 ± 2.5 | 0.4 ± 0.1 | 95.5 ± 1.7 |
| | 10 | 15.7 ± 2.5 | 0.3 ± 0.1 | 98.4 ± 0.5 |
| | 15 | 15.8 ± 4.2 | 1.4 ± 1.5 | 91.2 ± 7.4 |

Average ± standard deviation.

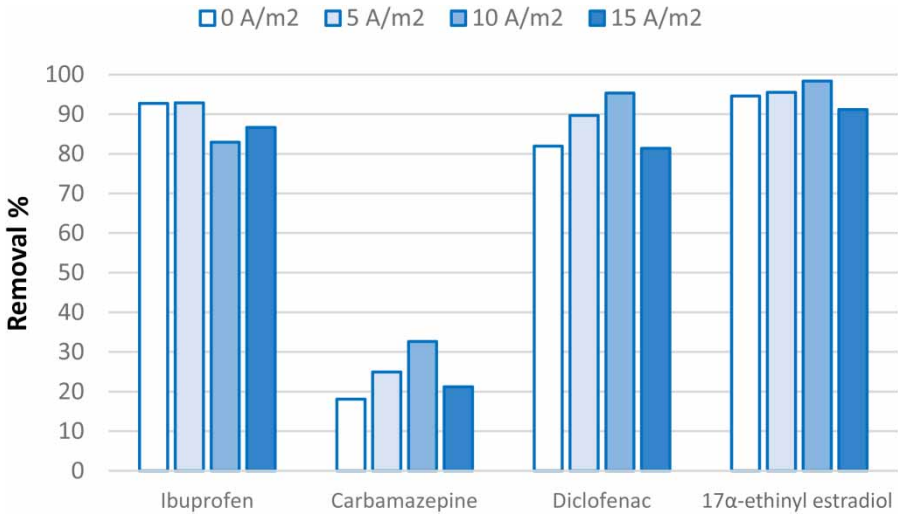



**Figure 4** | Average removal of each micro-pollutant for each CD applied in the eMBR.

for 0–15 and 5–15 A/m$^2$. Therefore, the application of EC, especially with high CD, negatively affected the removal of IB, probably because the electroflotation mechanism is the one that prevailed. It must also be considered that the removal percentages with conventional MBR were already very high. No other studies have been found that analyze the effect of CD variation on IB removal.

In the case of CBZ, the experimental average values showed an apparent improvement in removal for CD of 5 and 10 A/m$^2$. However, when applying the Wilcoxon statistical analysis, no significant differences ($p$-value $<0.05$) were found between any pair of CD values. Consequently, in our study, CD did not affect the removal of CBZ. Other authors report different behaviors: Borea *et al.* (2019), using conditions similar to those of the present work, found removal improvements for CBZ when increasing the CD, while Chen *et al.* (2020), in a study with real waters, found that there is no statistically significant influence of EC on the removal of CBZ.

In the case of DCF, there was an initial improvement in removal as the EC increased, obtaining mean values of 82.0, 89.7 and 95.3% for 0, 5 and 10 A/m$^2$, respectively. The Wilcoxon statistical analysis showed significant differences ($p$-value $<0.05$) between the results of 0–10 and 5–10 A/m$^2$, confirming the consistency of these data. Borea *et al.* (2019) and Chen *et al.* (2020) also obtained better DCF removals with eMBR compared to MBR. At high CD, in our investigation, the removal decreased appreciably between 10 and 15 A/m$^2$, with statistically significant average values, possibly due to the prevalence of the electroflotation mechanism for this CD.

Finally, the EE2 showed a behavior similar to the DCF, although less underlined. Highest elimination to 5 A/m$^2$ and decreases to 15 A/m$^2$, the mean values being statistically significant in all cases ($p$-value $<0.05$). No studies have been found in the literature that analyze the effect of CD on EE2 removal.

### 3.3. Removal of phosphorus

Figure 5 shows the evolution of the total phosphorus concentration in the influent and effluent of the eMBR, and the removal percentage achieved, during the four phases of the experimentation, with different CDs. The low yields of removal of PT measured in the changes from phase 2 to phase 3 and from phase 3 to phase 4, are due to the fact that during the CD changes, the eMBR sludge was replaced to avoid the presence of precipitated aluminum, following a stabilization period of a few days before adding EC again.

EC greatly improved phosphorus removal. The average removal percentage of TP was 97, 99 and 99%, for CDs of 5, 10 and 15 A/m$^2$, respectively, and only 40% when EC was not applied. These results are inconsistent with the values reported in multiple studies and were produced by the electro-oxidation reaction of the aluminum anode generating $Al^{3+}$ ions which bind the phosphorus present in the biomass, resulting in the precipitation as $(AlOH)_3(PO_4)_2$ and $AlPO_4$ or adsorption onto flocs as Al $(OH)_3$ (Bani-Melhem & Elektorowicz 2011; Hasan *et al.* 2014; Nguyen *et al.* 2016; Borea *et al.* 2017; Asif *et al.* 2020).

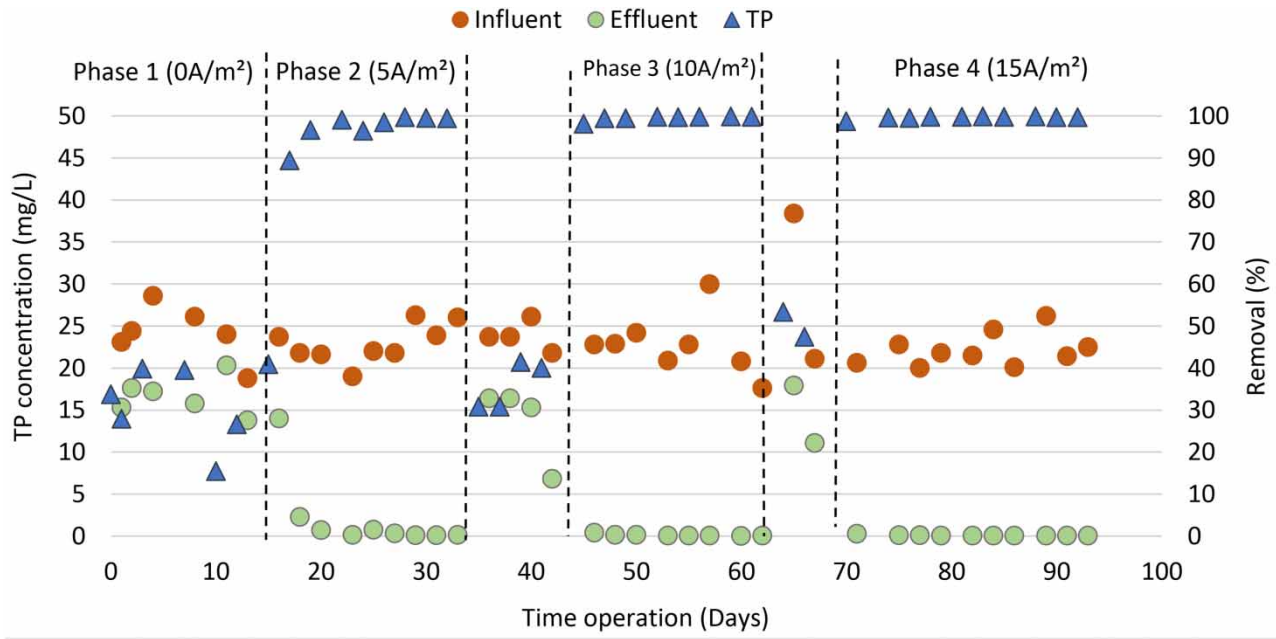



**Figure 5** | Evolution of the concentration of TP in the influent and effluent of the eMBR, and the percentage of removal achieved, during the 4 phases of the experimentation.

The application of the Kruskal–Wallis statistical analysis to the set of TP elimination results in the eMBR revealed that there was a statistically significant difference between the set of experiments performed with and without EC ($p < 0.05$). The Wilcoxon test showed that there are statistically significant differences between each pair of CD applied, except between the highest CDs, 10 versus 15 A/m$^2$. Hence, to achieve the maximum removal of TP, it would be sufficient to apply a CD of 10 A/m$^2$.

### 3.4. Membrane fouling

The fouling of the membrane is due to complex interactions between the materials contained in the mixed liquor of the MBR and the membrane, which cause the deposition, accumulation or adsorption of part of these materials on the surface and/or the internal pores of the membrane. The consequence is an increase in TMP during operation at constant permeate flow, which has an impact on the increase in energy consumption and the necessary physical and chemical cleaning (Guo *et al.* 2012; Lin *et al.* 2014).

The main responsible substances for membrane fouling are extracellular polymeric substances (EPS) and soluble microbial products (SMP), especially soluble proteins (Laspidou & Rittmann 2002; Hasan *et al.* 2012; Lin *et al.* 2014; Yang *et al.* 2018). It has been proven in multiple investigations that the application of EC in the MBR reduces the fouling of the membrane due to three electrochemical processes: (a) degradation/elimination of contaminants responsible for fouling due to EC mechanisms and direct and indirect oxidation; (b) electrophoresis, which occurs when the organic scale is negatively charged and can be dislodged from the membrane by moving toward the anode; (c) electroosmosis, which consists in the elimination of part of the hydration water from the activated sludge flocs, which reduces the size of the floc, its adhesion to the membrane and its specific resistance to filtration (Ibeid *et al.* 2015; Ensano *et al.* 2016; Borea *et al.* 2017; Asif *et al.* 2020).

Figure 6 shows the evolution of the TMP during phase 4 of experimentation, and Table 7 shows the average values of the membrane fouling rate (MFR) in the different phases and the concentrations in the activated sludge of MLSS, MLVSS, the MLVSS/MLSS ratio, EPS, SMP (proteins and carbohydrates) and the protein–carbohydrate ratio in SMP.

In phase 1, when operating in conventional MBR mode, the fouling of the membrane increased rapidly and progressively, the MFR reaching an average value of 1.79 kPa/day. By applying CD of 5, 10 and 15 A/m$^2$, an average MFR of 0.28, 0.44 and 0.34 kPa/day was obtained, which was 6, 4 and 5 times lower, respectively, than in the conventional MBR. In other words, the best results were achieved in phase 2, when applying a CD of A/m$^2$, and successive CD increase did not improve the fouling rate. This may be due to the fact that, although the increase in CD progressively decreased the concentration of EPS, the

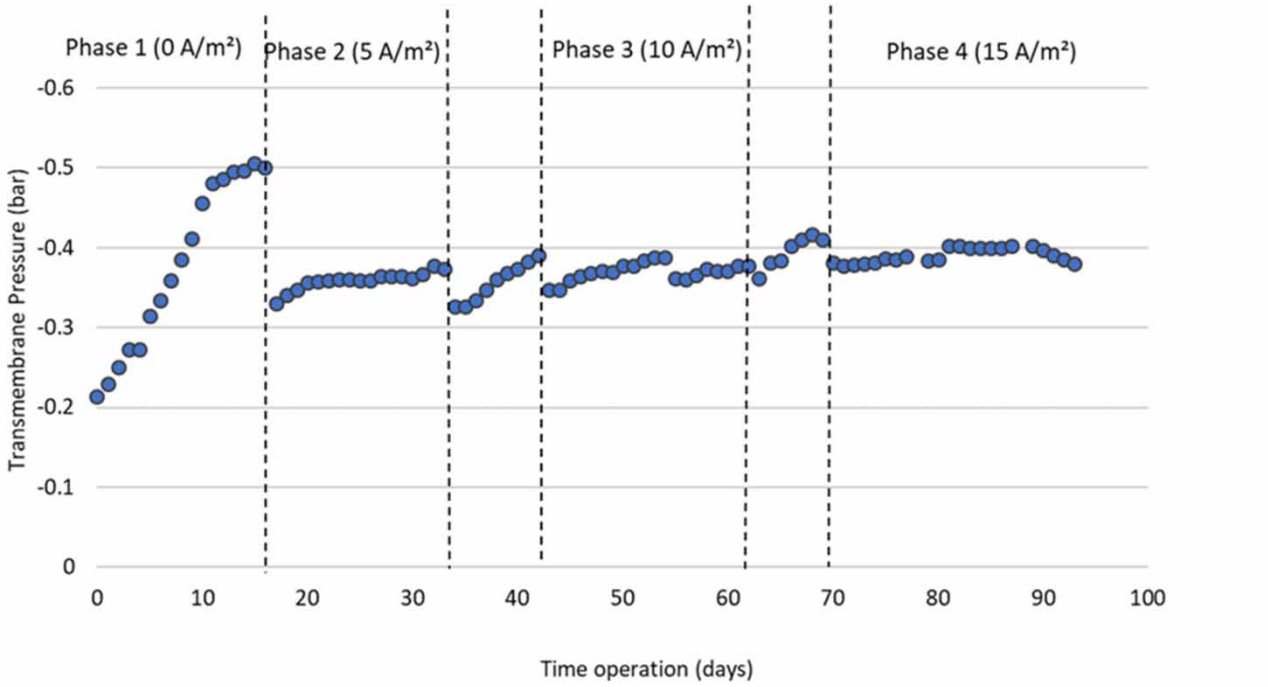



**Figure 6** | Transmembrane pressure's evolution across the different experimental phases.

**Table 8** | Average MFR values in the different phases and average concentration values in the activated sludge of MLSS, MLVSS, EPS and SMP, MLVSS/MLSS ratio and protein to carbohydrate ratio in SMP (SMPP/SMPc)

| Phase | MFR (kPa/day) | MLSS (g/L) | MLVSS (g/L) | EPS (mg/g MLVSS) | SMP[a] (mg/L) | MLVSS/MLSS | $SMP_P/SMP_c$ |
|---|---|---|---|---|---|---|---|
| 1 (0 $A/m^2$) | 1.79 | 3.2 ± 0.7 | 2.7 ± 0.5 | 135.4 ± 26.0 | 52.5 ± 13.1 | 0.84 ± 0.20 | 0.40 ± 0.15 |
| 2 (5 $A/m^2$) | 0.28 | 7.0 ± 3.4 | 4.3 ± 1.6 | 98.1 ± 23.3 | 46.8 ± 12.7 | 0.60 ± 0.12 | 0.34 ± 0.11 |
| 3 (10 $A/m^2$) | 0.44 | 7.8 ± 0.7 | 4.6 ± 0.5 | 79.1 ± 29.4 | 34.1 ± 13.2 | 0.59 ± 0.07 | 0.37 ± 0.10 |
| 4 (15 $A/m^2$) | 0.34 | 8.5 ± 2.8 | 3.7 ± 1.2 | 63.3 ± 15.4 | 35.4 ± 9.3 | 0.43 ± 0.13 | 0.53 ± 0.24 |

Values denote average ± standard deviation.
[a]Proteins and carbohydrates.

SMPs stabilized and the ratio of proteins to carbohydrates SMPP/SMPc (Table 8) increased from 10 $A/m^2$. In addition, the MLVSS/MLSS ratio decreased due to the increase in the presence of $Al^{+3}$ in the activated sludge, which could increase the inorganic fouling of the membrane (Wang *et al.* 2014). Similar behavior has recently been shown by Manica *et al.* (2020), who reported that with CD of 5 $A/m^2$, a lower MFR was obtained than with 15 $A/m^2$, which the authors attribute to the fact that a high CD deteriorates the characteristics of mixed liquor, resulting in a greater presence of soluble carbohydrates and an increased hydrophobicity of the EPS.

Consequently, the CD of 5 $A/m^2$ turned out to be the most suitable for mitigating the fouling of the membrane, and without a doubt the most interesting with regard to the energy-saving concept.

## 4. CONCLUSIONS

The UASB + MBR/eMBR combined system for urban wastewater treatment is a robust procedure that combines anaerobic and aerobic biological processes to achieve a high removal efficiency of organic matter, a rate of 94–98% for COD. The UASB reactor made the greatest contribution to the removal of COD, thus eliminating 75–85% of the initial COD. CD effects on the removal of COD were variable, they produced two opposite effects: on the one hand, filterability of the membrane improved reducing the organic matter removal through filtration; on the other hand, the removal of organic matter by EC and direct

and indirect oxidation increased. For CD of 5 and 10 A/m$^2$, the filterability effect remained, whereas at 15 A/m$^2$, the greatest removal was carried through oxidation within the reactor.

In this combined system, when working as conventional MBR, high global removal percentages have been achieved for IB (94.5%), DCF (87.1%) and EE2 (96.0), thus being this reactor the one that has contributed the most to the removal. The overall removal of CBZ has been 37.1%. Regarding this compound, the UASB reactor was the main contributor to its removal. CD effects on the removal of these micro-pollutants were variable as there were two opposite outcomes: on the one hand, EC and oxidation mechanisms augmented their elimination; on the other hand, the removal of the micro-pollutants could have decreased by dragging them to the surface by means of electroflotation mechanisms. As a result, the removal of IB was disadvantageous via EC: CBZ was not affected, however, in the case of DCF and EE2, removal increased at 5 and 10 A/m$^2$ and decreased at 15 A/m$^2$. Hence, it can be stated that there has been an optimal CD value for each micro-pollutant.

The effect of CD on phosphorus removal was very favorable. The application of 5 A/m$^2$ was sufficient to advance from a removal of 40% with the conventional MBR to a 97% removal with the eMBR. The application of higher CD values did not produce substantial changes in its removal, as with lower values, it was almost eliminated.

The effect of CD on the membrane fouling was also very favorable. The application of 5 A/m$^2$ allowed the reduction of the fouling rate by 6 times. Higher CDs application did make a difference in the fouling rate of the membrane.

In summary, this combined UASB + eMBR system achieved high removals of organic matter, total phosphorus, and some microcontaminants. Moreover, the MFR was significantly improved compared to a conventional MBR. The UASB reactor made a relevant contribution to the removal of organic matter, which will have repercussions in lowering energy consumption and production of sludge compared to a solely aerobic treatment. The foremost CD was 5 A/m$^2$, which resulted in substantial improvement of phosphorus and DCF and EE2 removal, as well as in a reduction of membrane fouling speed by six times, hence being clearly advantageous from the point of view of energy consumption.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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