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Abstract

Removal of pharmaceuticals from wastewaters is of particular importance nowadays. If biodegradable molecules can be nearly totally eliminated by biological treatments such as membrane bioreactor (MBR), many pharmaceutics are recalcitrant. To improve the removal of these micropollutants, an advanced oxidation process (AOP), based on TiO_2 photocatalyst, has been implemented on a recirculation loop on a 15-L MBR operated with a sludge retention time (SRT) of 30d and a hydraulic retention time (HRT) of 48h. This innovative process did not negatively impact the bacterial community of the MBR which maintained same a Total Suspended Solids (TSS) concentration of 5g.L^{-1} and a high carbon removal yield (> 92 %). For different flux densities tested (4, 17 and 40 W.m^{-2}), similar degradation efficiency was observed for two pharmaceuticals: ibuprofen (IBU) and carbamazepine (CBZ). Thus, a flux density of 4 W.m^{-2} was selected for the coupling. This configuration intensified the degradation of CBZ by a factor 10 (up to 28 % removal) in comparison with the MBR alone and the removal of IBU was maintained close to 99 %.

Keywords: pharmaceuticals, wastewater, photooxidation, membrane bioreactor, intensification.

1. Introduction

The Water Framework Directive [1] provides for policy measures to protect the environment and human health against risks tied to toxic pollution by setting objectives that aim to reduce or even eliminate discharges of specific substances and to achieve good ecological status. It thus makes water and sewage management and reuse a strategic economic, social and above all environmental challenge [2]. The issue is acutely focused on organic pollutants and pharmaceutical compounds [3]. With improved analytical techniques and lower limits of quantification, pollutants have now been detected in natural waters at concentrations between $ng.L^{-1}$ and $\mu g.L^{-1}$ [4–6]. The vast majority of these pollutants comes from wastewater treatment plant effluents, but some also come from hospital effluents [7,8]. Many of these substances readily is subject to biodegradation biodegrade and can therefore be degraded by biological-process treatment or by long periods in the environment. This is the case for many analgesics and some antibiotics [5,9,10]. However, there is another category of substances called persistent organic pollutants (POPs) that are more recalcitrant to conventional treatments. POPs cover a wide spectrum of drugs ranging from anti-inflammatories and antidepressants to antibiotics and beta-blockers [5,9], but all are suspected to be carcinogenic or endocrine disruptors, which makes them the focal challenge of pollution management measures.

Wastewater treatment plants (WWTP) based on biological processes (typically activated sludge) are still not fully effective in degrading organic micropollutants, especially POPs. The capacity of a biological treatment depends on both the properties of the molecules (chemical structure, sorption capacity, hydrophobicity, and son) and on the operational WWTP biological process parameters applied (hydraulic residence time, sludge residence time, etc.). Some pharmaceutical products, such as diclofenac or carbamazepine, are only partially eliminated with efficiencies below 40% while others, like ibuprofen, are relatively well eliminated (> 70%) [11,12]. Intensifying biological processes with technologies such as membrane bioreactor (MBR) has demonstrated better removal of most pharmaceuticals than activated sludge but still fails to completely remove all micropollutants [13,14].

In this context, many organic substances that are toxic or resistant to biological treatment continually get released into water bodies, soils, and other natural habitats [4]. A promising way forward is to complete this biological process with an advanced technology based on chemical oxidation. These advanced oxidation processes (AOPs) are widely recognized as very effective treatments for recalcitrant wastewater [15,16]. They are environmentally-friendly processes that hold the advantage of non-selectively

eliminating contaminant loads. Most AOPs are aqueous-phase oxidation processes based on producing hydroxyl radicals, the second strongest oxidant after fluorine, which have enough oxidizing power to destroy practically all types of organic contaminants [17,18]. AOPs generate large amounts of hydroxyl radicals under specific operating conditions. Studies have demonstrated the effectiveness of both advanced oxidation processes and solar photocatalytic oxidation [15,19].

Thus, a combination of biological and AOP processes could improve the all-round removal of micropollutants to achieve the abatement performance levels required under future regulatory constraints [20,21]. In the literature, several studies have tested the association of a biological process with an AOP to eliminate organic pollutants. In all these studies, the two processes are associated in series (sequentially) in two different configurations. The first configuration consists in positioning the oxidation process upstream as a pre-treatment [22,23]. The utility lies in the oxidation of biorecalcitrant substances, thus making the effluent biodegradable. The disadvantage is that it yields a complex effluent that contains pollutants at sometimes high concentrations along with suspended matter. This complex matrix could inhibit the specific degradation of the pollutants targeted by this treatment by increasing the competition between the substances. Increasing the quantity of total matter to be oxidized renders the treatment capacity of the oxidation process inadequate or even ineffective. It also negates the value of non-selective degradation, since in this case all pollutants—including biodegradables—will get oxidized during this step. The second configuration for coupling the two processes in series consists in positioning the AOP downstream of the biological process as a tertiary or quaternary treatment [21,24,25]. The objective here is to improve the biological treatment by oxidizing the substances that have been partially or not degraded. The challenge with this association is to degrade molecules that are at very low concentrations in large volumes of water and ensure that they are totally mineralized and thus not released into the environment. The innovative association proposed in this paper consists of a compromise between these two modes of association in a way that exploits the advantages of each. The biological process is a MBR because of its high pharmaceutical removal performance and its suspended solids-free outlet. The AOP is based on titanium dioxide (TiO_2) photocatalysis which non-selectively but very efficiently degrades organic pollutants such as pharmaceuticals. The concept is based on coupling the two processes, where the AOP is not staged in series with the MBR but in a recirculation loop on the MBR itself. In this configuration, the final objective of the AOP is not to fully mineralize the POPs leaving the MBR but to partially transform them into biodegradable substances that are then eliminated when they are re-streamed back into the MBR [26]. The purpose of this combined technological configuration is to obtain a stronger synergistic effect than the simple sequential implementation of the two processes (MBR + AOP).

To evaluate the performance of the coupled reactors, the progress of two pharmaceutical molecules were tracked through the process: ibuprofen (IBU) and carbamazepine (CBZ). These two molecules were chosen as they are both widely encountered in WWTPs and in freshwaters [8,27,28] but have different toxicity profiles and different biodegradability levels [29,30]. Ibuprofen is highly biodegradable whereas carbamazepine is biorecalcitrant. Many studies on titanium dioxide photocatalysis for pharmaceutical wastewater removal have employed these same molecules for the same reasons [31].

The aim of this study was to prove the feasibility and utility of this mode of process association by investigating whether recirculating the effluent in an oxidation process increases MBR efficiency. For that purpose, pharmaceutical removal rates in a 15-L MBR alone versus a MBR coupled with a photooxidation process were compared. The MBR was operated with a sludge retention time (SRT) of 30d and a hydraulic retention time of 48h. The photo-oxidation process was tested at several flux densities.

2. Material and Methods

2.1. Standardized Synthetic effluent

Carbamazepine (CBZ) and ibuprofen (IBU) were purchased from Sigma–Aldrich MO (100% purity; Sigma-Aldrich, MO). A concentrated solution was prepared weekly in tap water at a concentration of 50 $\mu g.L^{-1}$ for CBZ and 400 $\mu g.L^{-1}$ for IBU.

The concentrated synthetic wastewater was composed of peptone (4800 $mg.L^{-1}$), meat extract (3300 $mg.L^{-1}$), K_2HPO_4 (210 $mg.L^{-1}$), NaCl (52.5 $mg.L^{-1}$), $CaCl_2$ (120 $mg.L^{-1}$), $MgSO_4$ (60 $mg.L^{-1}$), NH_4Cl (750 $mg.L^{-1}$) and NaOAc (600 $mg.L^{-1}$). These substances have been diluted in tap water, corresponding to a chemical oxygen demand (COD) of 1000 mg L−1, a total N (TN) content of 120 mg L−1 and a total P (TP) content of 10 mg L−1. pH was maintained at 7.2. The composition of this standardized synthetic effluent based on OECD guidelines which is characteristic of wastewater from wastewater treatment plants, is commonly used in the literature [32]. A standardized synthetic effluent makes it possible to carry out a series of experiments over a long period of time with reproducible feeding conditions and to be able to compare the performance of the system from one experiment to another.

2.2. Experimental set-ups

2.2.1. Membrane bioreactor

A 15 L MBR equipped with a Rushton turbine (200 rpm) was operated at a hydraulic retention time $HRT_{MBRalone}$ = 48 h and a sludge retention time (SRT) of 30 d (**Fig. 1**). At the initial start-time, the MBR was

filled with activated sludge sourced from a real WWTP (Perpignan, France) with a total suspended solids (TSS) concentration of 2.5 $g.L^{-1}$. A tubular ceramic membrane (Membralox®, Pall Exekia, France) with surface area of 0.0055 m^2 and pore size of 0.2 µm was positioned in an external module. Tangential velocity in the membrane was set at 4.5 $m.s^{-1}$. Probes were used to monitor temperature, dissolved oxygen and pH. pH was adjusted to 7 by adding NaOH at the beginning. Cycles of 5 min aeration (dissolved oxygen of 6 $mg_{O2}.L^{-1}$) / 40 min without aeration were used to create aerobic/anoxic conditions for the nitrification and denitrification steps [33].

The MBR was continuously fed at a flow rate of Q_{IN} = 7.5 $L.d^{-1}$ (**Fig. 1**). This inflow was composed of 1 $L.d^{-1}$ of concentrated synthetic solution, 1 $L.d^{-1}$ of concentrated micropollutant solution, and 5.5 $L.d^{-1}$ of tap water. Consequently, composition at the MBR infeed was: 1000 $mg.L^{-1}$ chemical oxygen demand (COD), 120 $mg.L^{-1}$ total nitrogen (TN) and 10 $mg.L^{-1}$ total phosphorus (TP). Inlet concentrations of micropollutant were 7 $\mu g.L^{-1}$ CBZ and 53 $\mu g.L^{-1}$ IBU. These concentrations were chosen to be representative of real concentrations measured in thousands of WWTP in the EU [34] and across the world [14].

After a 70 d adaptation phase, the MBR was considered to be in a steady sate (TSS and outlet concentrations were constant). Every two or three days, 20 mL samples of the feed solution and permeate were taken at end of the anoxic phase and frozen at -20 °C until analysis to determine COD, TN, NH_4^+, NO_2^- and NO_3^- concentrations. Samples of sludge (evenly taken away at a flow rate of Q_S = 0.5 $L.d^{-1}$) were also collected at regular intervals to measure TSS and volatile suspended solids (VSS).

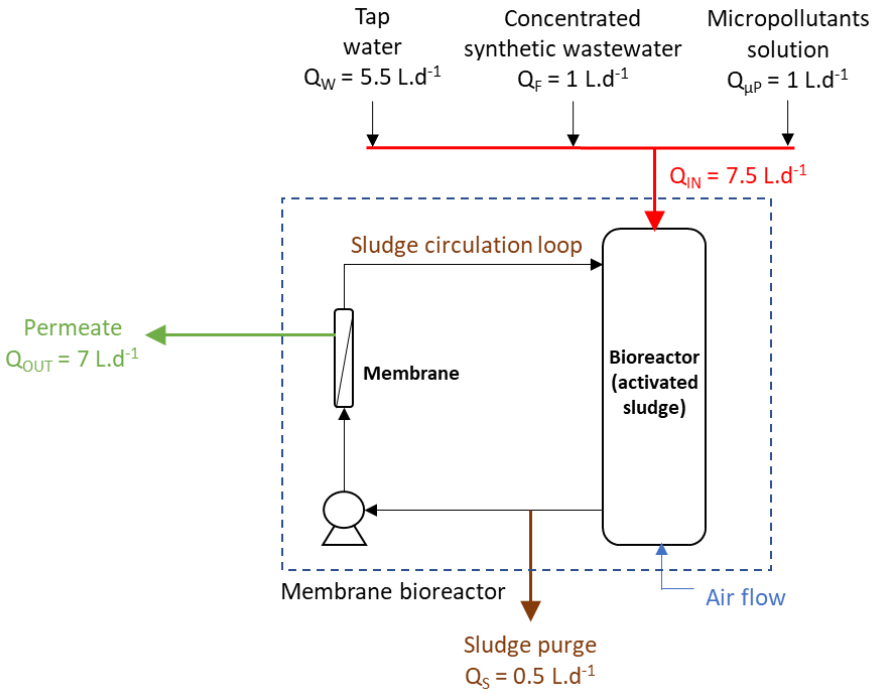


Figure 1: Synoptic of the experimental set up of the membrane bioreactor.

2.2.2. Photoreactor pilot

The lab-scale photoreactor (**Fig. 2**) was composed of a single closed 2 L flat-panel (25 x 45 x 2 cm) parallelepiped-shaped reactor with a stainless-steel base and a UV-transparent (91 % UV transmission) PMMA plate covering the front. Irradiance source was an artificial LED UV panel of the same surface area as the tank to deliver uniform irradiance. This LED UV panel was set 2 cm from the PMMA surface. Irradiance was delivered in a very narrow spectrum centered around 365 nm. After calibration with a MU-200 UV sensor (Apogee Instrument, Logan, UT, USA), radiant flux density at the reactor surface was controllable and adjustable between 5 and 85 $W.m^{-2}$. As the solar UV flux density varies from 0-50 $W.m^{-2}$, three flux densities representative of the solar irradiation range were selected: 4, 17 and 40 $W.m^{-2}$ [17].

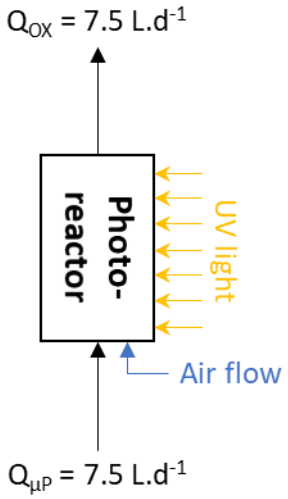


Figure 2: Synoptic of the experimental set up of the photoreactor.

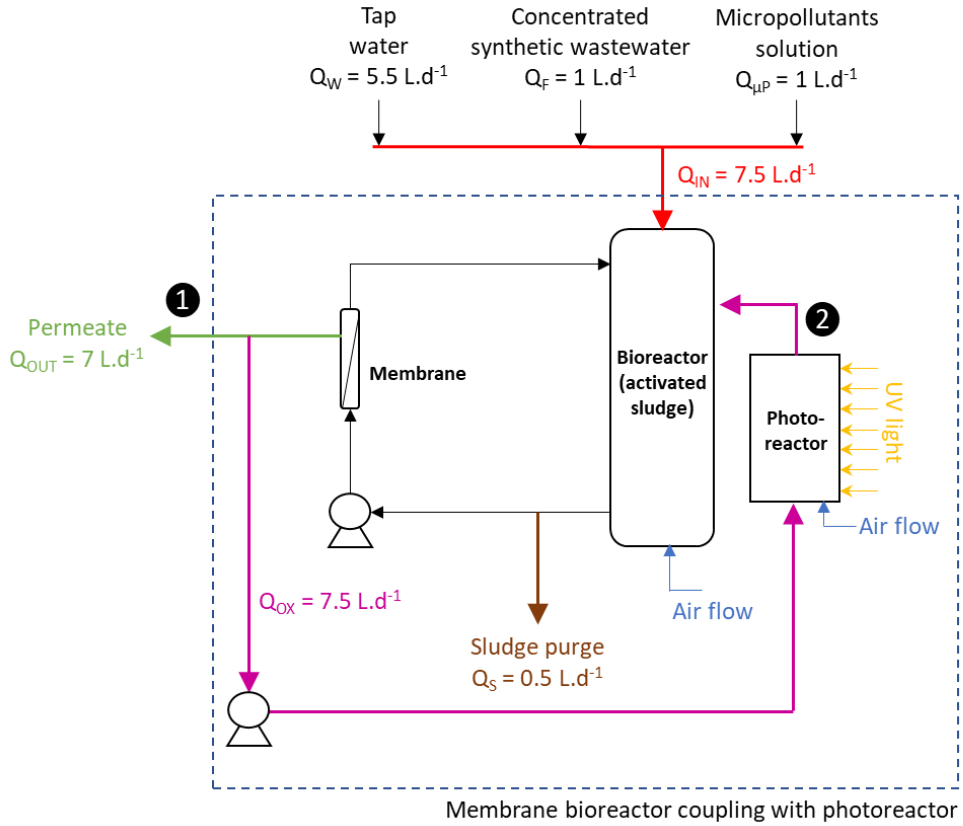
Titanium dioxide (TiO_2) was chosen as it is one of the most attractive catalysts for environmental remediation [35], used in its photosphere form, i.e. 45 µm (range: 5 µm–85 µm) TiO_2-coated glass microspheres. The advantage of this form is that it floats (0.22 $g.L^{-1}$ density) and is therefore easier to separate from treated water. The optimal photocatalyst concentration corresponds to total absorption of the radiation inducing the fastest kinetics [36]. Preliminary tests (data not shown) run with varying photosphere concentrations concluded that a concentration of 5 $g.L^{-1}$ maximized the pollutant degradations kinetics. Fresh catalyst was used at the start of each experiment. The photospheres were homogenized in the water by pressurized airflow pumped into the tank bed via five holes evenly spaced across the width.

The photoreactor, filled with 2l of effluent, develops a light capture surface of 0.12 m^2. The pilot was used in continuous mode, driven for the inlet by a peristaltic pump (Watson Marlow 205U) at 7.5 $L.d^{-1}$ (HRT_{OX} = 6.4 h) for the micropollutant solution inflow ($Q_{\mu P}$). For the outlet, just overflow/water-levelling was used (Q_{OX}). To achieve the separation between the catalyst and treated water, i.e. avoid release into the sewer system and maintain its concentration in the photoreactor, we purpose-engineered a flotation system composed of a reverse funnel.

2.2.3. Coupling the membrane bioreactor with the photoreactor

The MBR was first inoculated in the same way as presented in 2.2.1. After the adaptation phase, the photoreactor was hydraulically connected (UV turned off) with the MBR by a recirculation loop at a flow rate of 7.5 $L.d^{-1}$ via the same peristaltic pump (Watson Marlow 205U) (**Fig. 3**). The flows previously stated for the MBR (Q_F, $Q_{\mu P}$, Q_S, Q_{OUT}, **Fig. 1**) and the photoreactor (Q_{OX}, **Fig. 2**) were kept the same, leading to the same flows for the final coupled system (**Fig. 3**). In this configuration, the HRT of the MBR ($HRT_{MBRcoupled}$) was 24 h with a global flow of 15 $L.d^{-1}$.

After 8 days of running without oxidation, the UV lamp of the photoreactor was turned on. The same sampling procedure as for the MBR was repeated for global parameter measurements (COD, TN, NH_4^+, NO_2^-, NO_3^-, TSS, VSS).



Membrane bioreactor coupling with photoreactor

Figure 3: Synoptic of the coupling of the membrane bioreactor with the photoreactor. Numbers in black discs are the sampling points used to follow the pharmaceuticals degradation.

2.3. Analytical methods

2.3.1. Sludge characterization

The TSS and VSS contents of the activated sludge were measured according to standard methods 2540D and 2540E [37].

2.3.2. Chemical characterization of the wastewater

COD, TN, NH4-N, NO2-N, NO3-N, and TP concentrations were determined using to HACH Kits (LCK tubes) with a HT200S thermostat (HACH) and a DR3900 spectrophotometer (HACH, Loveland, CO, USA).

2.3.3. Pharmaceutical compounds analysis

When the reactors were independent, samples were taken at the outlet (Q_{OUT}) of both the MBR (**Fig. 1**) and the photoreactor (**Fig. 2**). When the reactors were coupled together, samples were taken at position ❶ at the outlet of the MBR and position ❷ at the outlet of the photoreactor (**Fig. 3**). Three samples were taken at steady state on 3 different days.

A volume of 150 mL was sampled then filtered through a 0.4 µm pore-size hydrophilic filter and mixed with thiosulfate before being frozen at -20°C for storage pending dispatch to the COFRAC-accredited Carso laboratory (France) for analysis. Concentrations were monitored at the lab by liquid chromatography–tandem mass spectrometry (LC-MS/MS). Limits of quantification were 5 $ng.L^{-1}$ for CBZ and 100 $ng.L^{-1}$ for IBU. All analyses were done in triplicate, and all results are average of the triplicate measures.

3. Results and Discussion

3.1. Carbon, nitrogen and phosphorus removal performances

As the main function of the MBR is to remove COD, TN and TP, the all-round performances of the MBR were investigated with the photoreactor configured in coupled mode with the UV light turned off and then turned on (inducing the photocatalysis process) as described in section 2.2.3.

The apparent removal efficiencies (E) of the MBR were calculated as follows:

$$E = \frac{C_{IN} - C_{OUT}}{C_{IN}} . 100 \qquad eq.1$$

where C_{IN} and C_{OUT} are concentration of the target parameter (COD, TN or TP) at the inlet and outlet (position ❶), respectively **(Fig.3)**.

Table 1: Apparent removal efficiency (E) for COD, TN and TP in coupling MBR-photoreactor without and with oxidation step at 8.5 W.m-2

	Apparent removal (E %)	
	With UV lamp OFF	**With UV lamp ON**

COD	92.3 ± 3.4	95.0 ± 0.7
TN	38.6 ± 15.5	56.8 ± 5.9
TP	25.3 ± 14.6	41.4 ± 25.4

Mean removal of COD, TN and TP measured at steady state is shown in **Table 1**. Coupling the oxidation step with the MBR had no significant impact on COD and TN removal. For TP, the standard deviations were high due to some variations observed at the MBR outlet, making it is difficult to reach a firm conclusion on this parameter. The fact that these all-round performances were not negatively impacted by recirculating oxidized permeate into the MBR means that the photooxidation process had not impacted the microbial community for the duration of the oxidation step (20 days). It could be concluded that no toxic by-products were formed in the oxidative conditions tested, as even though the duration of this experiment was relatively short, there was no decrease in COD, TN and TP removal under any of the other oxidative conditions tested in this study. This result lays the foundations to implementing the innovative process proposed in this paper as a way to improve micropollutant removal.

3.2. Removal of pharmaceuticals in the membrane bioreactor alone

The MBR was first run independently in continuous mode at a flow of 7.5 $L.d^{-1}$ and an inlet concentration of 7 $\mu g.L^{-1}$ CBZ and 53 $\mu g.L^{-1}$ IBU to give a baseline reference (**Fig 1.**). The goal was to determine its removal efficiencies for the two pharmaceuticals in order to compare them with the removal efficiency of the coupled system.

At steady state, the average of triplicate outlet concentration measurements was 6.8 (±2.0) $\mu g.L^{-1}$ for CBZ and 1.1 (±0.7) $\mu g.L^{-1}$ for IBU. Comparison of these final concentrations with the initial 'reference' concentrations finds that the MBR did not degrade CBZ but was able to degrade IBU by a factor of 50.

To overcome the difference in initial concentrations between CBZ (7 $\mu g.L^{-1)}$ and IBU (53 $\mu g.L^{-1}$), the apparent removal efficiencies (E_{MBR}) of the MBR were recalculated using *Eq.1* and considering C_{IN} as the inlet micropollutant concentration and C_{OUT} as the outlet micropollutant concentration (see **Fig. 1**).

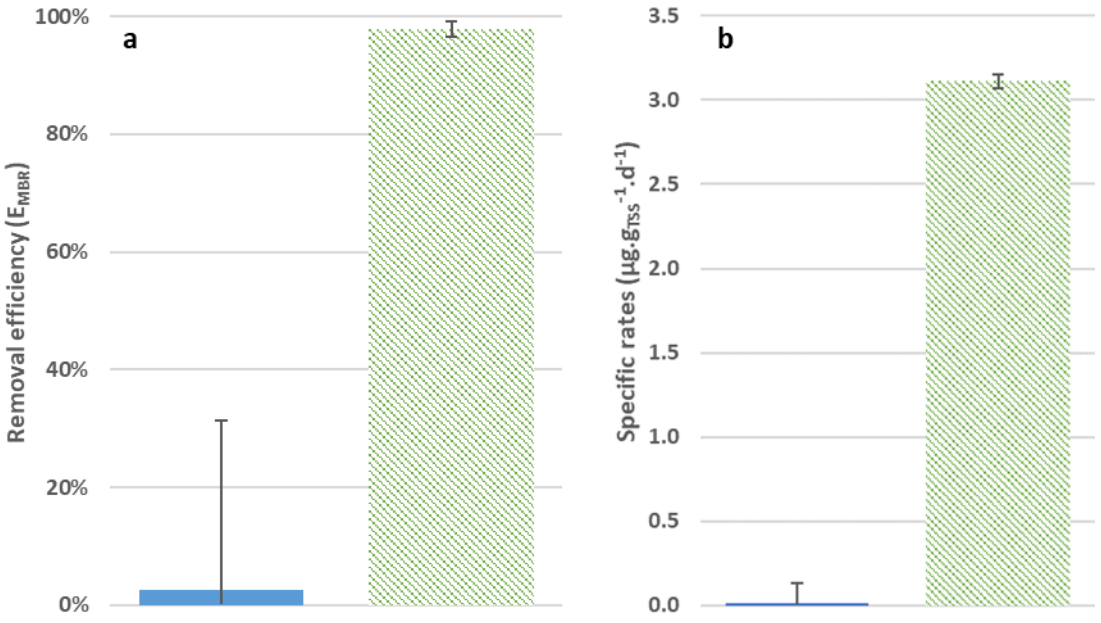


Figure 4: carbamazepine [plain blue] and ibuprofen [green zebras], removal efficiencies (left) and specific rates (right) by the membrane bioreactor alone.

The MBR alone thus had a removal efficiency of no more than 3 % (±29) for CBZ but 98 % (±1) for IBU (**Fig. 4a**). These figures are in the range of value reported in the literature that finds CBZ to be biorecalcitrant (E between -42 % and 51 %) and IBU to be readily biodegradable (E between 73 % and 100 %) [14,38,39].

To push the analysis further, the specific biodegradation rate (r_{MBR}, $\mu g.g_{TSS}^{-1}.d^{-1}$) and the first-order biodegradation rate constant of (k_{biol}, $L.g_{TSS}^{-1}.d^{-1}$) were calculated. As sorption of both IBU and CBZ can be neglected (<5%), [40, 41], the specific biodegradation rate has been estimated in steady state as follows:

$$r_{MBR} = \frac{Q_{IN}.(C_{IN} - C_{OUT})}{V_{MBR}.C_{TSS}} \qquad eq.2$$

where C_{TSS} is sludge concentration (5 $g.L^{-1}$) and V_{MBR} is volume of MBR. With the same assumption of negligible sorption, the biodegradation rate constant was estimated as follows:

$$k_{biol} = \frac{Q_{IN}.(C_{IN} - C_{OUT})}{V_{MBR}.C_{TSS}.C_{OUT}} \qquad eq.3$$

Comparison of the specific biodegradation rates of IBU and CBZ (**Fig. 4b**) shows that biodegradation was 300 times faster for IBU than for CBZ (3.11 ±0.04 $\mu g.g_{TSS}^{-1}.d^{-1}$ for IBU *vs*. 0.01 ±0.12 $\mu g.g_{TSS}^{-1}.d^{-1}$ for CBZ). This is mainly due to the biodegradability of the IBU which was very sensitive to microbial activity in the MBR and accentuated by the fact that the IBU was more concentrated in the feed effluent (C_{IBU} = 53 $\mu g.L^{-}$

266 [1] *vs* C_{CBZ} = 7 µg.L^{-1}), whereas CBZ, due to its persistent nature, proved very resistant to biological
267 degradation.
268 This is confirmed by the values of the biodegradation rate constants, for which the ratio between IBU
269 (2.76 ± 0.03 L.g_{TSS}^{-1}.d^{-1}) and CBZ (1.6x10^{-3} ± 0.24 L.g_{TSS}^{-1}.d^{-1}) was more than 1500. According to the
270 classification of [42], CBZ can be considered a 'hardly biodegradable' compound (k_{biol} < 0.1 L.g_{TSS}^{-1}.d^{-1}) and
271 IBU as a 'highly biodegradable' compound (1 < k_{biol} < 5 L.g_{TSS}^{-1}.d^{-1}). In the literature, depending on
272 operating conditions (HRT and SRT), k_{biol} in a MBR is always < 0.1 L.g_{TSS}^{-1}.d^{-1} for CBZ and in a range from 8
273 to 38 L.g_{TSS}^{-1}.d^{-1} for IBU [40].
274

275 ### 3.3. Removal of pharmaceuticals in the photoreactor alone

276 The photoreactor (**Fig. 2**) was operated in a continuous mode at a flow rate of 7.5 L.d^{-1} under three
277 different flux densities, i.e. 4 W.m^{-2}, 17 W.m^{-2} and 40 W.m^{-2}. This range of flux densities (4 to 40 W.m^{-2})
278 corresponds to the values of solar radiation during a standard day, and thus serves to test the utility of
279 using solar photooxidation processes for future real-world applications. As the work of Reoyo-Prats [44]
280 has shown that, over the range considered, the concentration level has a negligible influence on the rate
281 of degradation, these experiments used the concentrated solution of micropollutants (50 µg.L-1 for CBZ
282 and 400 µg.L-1 for IBU) in order to obtain a better accuracy of the measurements.
283 Oxidation efficiency (E_{OX}) was calculated according to the following equation:

284 $$E_{OX} = \frac{C_{\mu P} - C_{OX}}{C_{\mu P}} . 100 \qquad eq.4$$

285 where $C_{\mu P}$ and C_{OX} are micropollutant concentration at the inlet and outlet of the photoreactor,
286 respectively (**Fig.2**).
287

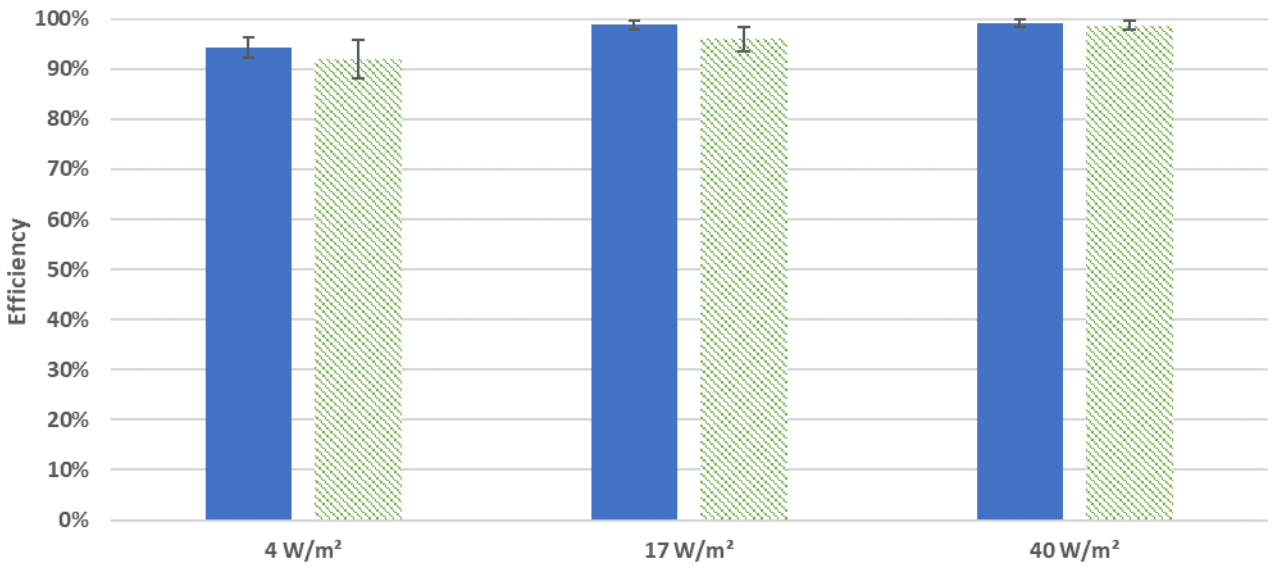


Figure 5: carbamazepine [plain blue] and ibuprofen [green zebras] removal efficiency by the photoreactor alone for different flux densities.

Fig 5 plots the influence of flux density on oxidation efficiency**.** Both CBZ and IBU were nearly totally degraded, with removal efficiencies higher than 90 % whatever the flux density applied. This confirms that contrary to the biodegradation process, photooxidation is non-selective [16,43]. **Fig. 5** shows that even a flux density as low as 4 $W.m^{-2}$ is enough to degrade the two molecules with removal efficiencies of 94 ± 2 % for CBZ and 92 ± 4 % for IBU. At 40 $W.m^{-2}$, these removal efficiencies increased to 99 ± 1 % for CBZ and 98 ± 1 % for IBU. These only slight differences in removal efficiencies between 4 and 40 $W.m^{-2}$ show there is little interest in consuming 10 times more electricity to slightly better degrade the two micropollutants. These results show that the operating conditions and particularly HRT in the photoreactor were sufficient to degrade almost all the substances. In other words, even when flux density was low, the contact time was enough to degrade the target molecules. For this configuration, the contact time of around 6 hours was very long with regard to the experimental conditions applied. This finding is in agreement with the literature on photoreactors operating in batch mode showing very significant degradation of these two micropollutants [44] or other persistent compounds [19] after only a few hours of treatment.

The removal efficiencies were similar and very high for both selected molecules—there was no preferential degradation of one molecule over the other. The difference, which in accordance with the literature is in favor of IBU [44], was not very significant here. Photodegradation experiments carried out on the compounds alone showed that IBU photodegraded more readily than CBZ (10 % – 20 % difference depending on the matrix) whereas the compounds in a cocktail were photodegraded at identical

efficiencies. These results confirm the non-selective nature of the photoreaction process, at least for the selected molecules. Note that the initial concentrations of CBZ and IBU were very different (IBU was 8 times more concentrated than CBZ) yet their removal efficiencies were identical, which implies that the degradation rate was around 8 times higher for IBU than CBZ. However, given the non-selectivity of photodegradation, this result indicates that degradation rate was concentration-dependent and was almost proportional to the quantity of carbonaceous matter in the substances. In other words, it shows that the process degraded these two molecules indiscriminately and at the same removal efficiency.

3.4. Coupling the membrane bioreactor with the photoreactor

The photooxidation process was then associated with the MBR. Contrary to usual practice in the literature, this association was not in series where the oxidation process acts as a pre-treatment or post-treatment. The configuration proposed here, as illustrated in **Fig. 3**, positions the oxidation process on the MBR recirculation loop, so the oxidation step acts both as a post-treatment to degrade the biorecalcitrant molecules at the outlet of the MBR and as a pre-treatment that oxidizes these compounds to make them more biodegradable for the biological process.

Based on the results obtained for photooxidation alone (Section 3.3.), the lowest flux density of 4 $W.m^{-2}$ was chosen as it assured the best removal-to-energy consumption trade-off. The flow rates of 7.5 $L.d^{-1}$ were kept for both reactors (**Fig. 3**) in order to allow direct comparisons. The initial concentrations (C_{IN}) were kept at 7 $\mu g.L^{-1}$ for CBZ and 53 $\mu g.L^{-1}$ for IBU.

To assess the efficiency of the coupling processes (E_{MBR+OX}) for micropollutant elimination, the all-round removal efficiency was calculated between the inlet (C_{IN}) and the outlet (C_{OUT}) at position ❶ of the global coupled system (**Fig. 3**.), according to *Eq.1* as previously**.**

The effective degradation capacity of the two coupled processes was estimated using specific degradation rate (r_{MBR+OX}) based on the mass balance between the inlet and outlet of the overall system (**Fig. 3**):

$$Q_{IN} \cdot C_{IN} = Q_{OUT} \cdot C_{OUT} + r_{MBR+OX} \cdot V_{MBR+OX} \cdot C_{TSS} \qquad eq.5$$

with $V_{MBR+OX} = V_{MBR} + V_{OX}$

So, the specific degradation rate (r_{MBR+OX}) was:

$$r_{MBR+OX} = \frac{Q_{IN} \cdot C_{IN} - (Q_{OUT} \cdot C_{OUT} + Q_S \cdot C_S)}{V_{MBR+OX} \cdot C_{TSS}} \qquad eq.6$$

As $C_{OUT} = C_S$ at steady state and $Q_{OUT} + Q_S = Q_{IN}$, *eq.6* can be simplified as follows:

$$r_{MBR+OX} = \frac{Q_{IN} \cdot (C_{IN} - C_{OUT})}{V_{MBR+OX} \cdot C_{TSS}} \qquad eq.7$$

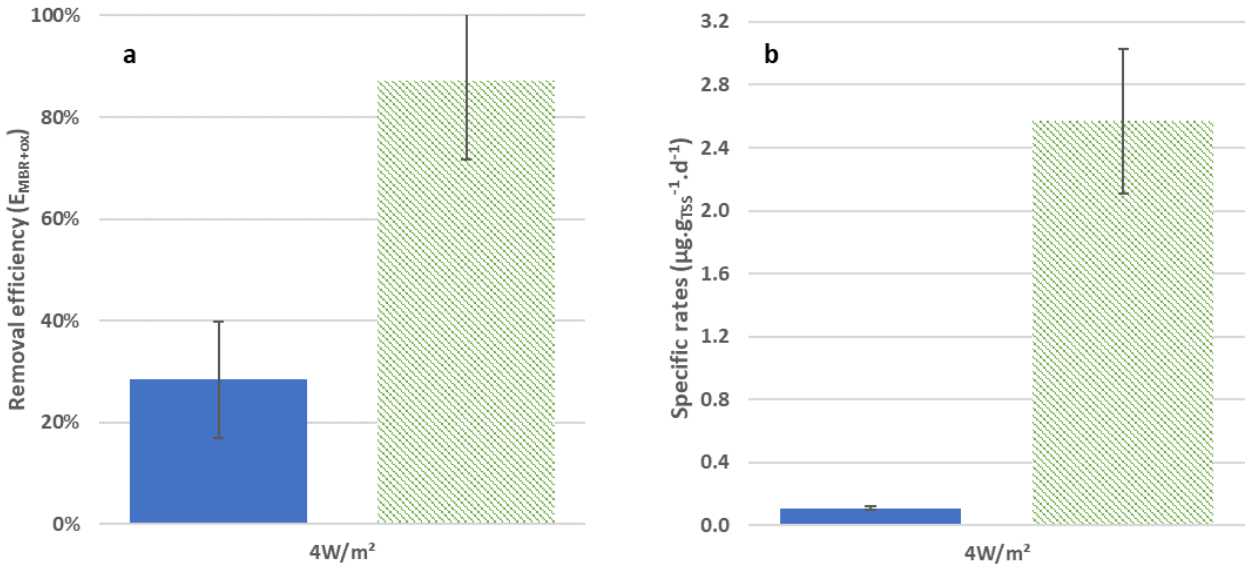


Figure 6: carbamazepine [plain blue] and ibuprofen [green zebras] removal efficiencies (left) and specific rates (right) by the coupling of the membrane bioreactor with the photoreactor at 4W/m².

The values for E_{MBR+OX} and r_{MBR+OX} are reported in **Fig. 6a** and **Fig. 6b,** respectively, for both IBU and CBZ. In this coupled configuration, CBZ was partially degraded (E_{MBR+OX} = 28 ± 11 %) and IBU was almost totally degraded (E_{MBR+OX} = 87 ± 15 %).

On the one hand and as expected, IBU was nearly totally degraded, as its removal reached 98 ± 1 % for MBR alone (**Fig. 4a**). Both removal efficiency and specific degradation rate were not significantly different between them. The slight decrease in degradation rate observed between the MBR alone (r_{MBR} = 3.11 ± 0.04 µg.g_{TSS}^{-1}.d^{-1}, **Fig. 4b**) and the coupled process (r_{MBR+OX} = 2.57 ± 0.46 µg.g_{TSS}^{-1}.d^{-1}, **Fig. 6b**) can mainly be explained by the fact that the calculation for r_{MBR+OX} considers the volumes of both reactors whereas the calculation of $r_{MBRCoupled}$ only considers the volume of the MBR. For this highly biodegradable compound, there was no positive or negative impact due to the oxidation process, which means that the experimental operating conditions for the coupled system in terms of residence time and microbial community were sufficient to degrade biodegradable substances.

On the other hand, CBZ is more persistent and thus poses a different challenge. Coupling the MBR with the photooxidation process allowed to improve the removal efficiency from less than 3 % for the MBR alone (**Fig. 4a**) to up to 28 % with the MBR coupled to the photoreactor (**Fig. 6a**). This improvement was expected, as the photoreactor alone had already shown a high removal efficiency of 94% (**Fig. 5**), in the tested oxidation conditions (flux density = 4 W.m^{-2}, HRT_{OX} = 6.4 h). Note, however, that these performances were achieved with a low-capacity oxidation process, as the HRT was 3.5 times longer in the MBR than in

the photoreactor. The specific degradation rate increased from r_{MBR} = 0.01 ±0.12 µg.g_{TSS}^{-1}.d^{-1} with the MBR alone (**Fig. 4b**) to r_{MBR+OX} = 0.11 ±0.01 µg.g_{TSS}^{-1}.d^{-1} in the coupled-process configuration (**Fig. 6b**), which means that the ratio between degradation rates of IBU and CBZ was increased by a factor 10. Coupling the photoreactor to the MBR thus appears to increase the selective degradation of biorecalcitrant molecules. It is difficult to compare our findings with published literature as there are almost no reports on coupling an MBR with a photooxidation process. Only one study that described an integrated MBR with TiO_2 photocatalysis for wastewater treatment was found [45]. The authors showed up to 95% removal efficiency for CBZ, but the initial CBZ concentration was very high (10 mg.L^{-1}) and so the final concentration was always close to 1 mg.L^{-1}. Moreover, their study was not operating in continuous mode but in sequenced batch mode. Most other work in the literature proposes a combination of these two processes associated in series.

The oxidation process positioned in pre-treatment seems to be effective for highly-concentrated effluents [46, 47] and effluents containing mainly persistent compounds (pesticides, PAHs) [23,48]. Its utility lies in the partial mineralization of the native molecules in order to make them biodegradable and consequently eliminable by the biological process. However, the results are inconclusive for effluents with low concentrations of micropollutants or effluents loaded with suspended solids. Indeed, these conditions not only hinder irradiation of the catalysts but also inhibit the photodegradation process because the TSS compete with the carbonaceous matter to be degraded [44].

Concerning the oxidation process positioned as a post-treatment, Leyva-Díaz et al. [24] showed that removal performances were almost independent of type of AOP used (Fenton, H_2O_2, photocatalysis). Work on these associations (oxidation process as a post-treatment of a biological process) in continuous mode amounts to a few dozen publications that mainly deal with low-concentration effluents. The studies tend to show that the native molecules are partially affected but that the association has a strong impact on toxicity [49] but also on biodegradability [22,25] and on the composition of process by-products. This tendency was due to the non-selective nature of oxidative degradation technologies that indiscriminately degrade all carbonaceous molecules. To complete the degradation of the by-products resulting from the oxidative treatment, Leyva-Díaz et al. [24] proposed a combined MBR-POA-MBR configuration that allows to reduce the toxicity of persistent native compounds by returning the oxidized effluent to a second biological process.

These solutions involving additional treatments may be efficient but they are also expensive. A recirculating combination, as proposed in this article, offers a compromise between pre-treatment and post-treatment configurations without additional steps. It holds the advantages of post-treatment by

attacking the residual molecules of the biological treatment—which are by definition persistent—and thus allowing to complete degradation performance by returning the effluent made biodegradable back into the MBR. Experiments in the literature are generally conducted with mature energy-intensive processes (ozonation [25], fenton [22]) or by oversized homogeneous or heterogeneous photocatalysis (high irradiation conditions for small volumes, or very long residence times [50]. Under these conditions, they can non-selectively increase the removal rates by several dozen percent COD or BOD [22,25]. However, they still do not preferentially target persistent compounds, which makes the system less efficient (high cost or oversized) for removing specific POPs.

3.5. Intensification of membrane bioreactor performance: synergic effect of the photoreactor

To highlight any potential synergy enabled by the proposed coupling, removal efficiency ($E_{MBRCoupled}$) and specific degradation rate ($r_{MBRCoupled}$) were estimated for the MBR alone but operating within the overall system, i.e. coupled with the photoreactor, in order to compare the results against the values obtained for the MBR alone (*eq.1* and *eq.2*) and the coupling process (*eq.1* and *eq.7*).

Removal efficiency ($E_{MBRCoupled}$) was calculated as follows:

$$E_{\mathrm{MBRCoupled}} = \frac{C_{IN} + C_{OX} - C_{OUT}}{C_{IN} + C_{OX}} \cdot 100 \qquad eq.8$$

The calculation of $r_{MBRCoupled}$, i.e. the specific rate of the MBR intensified by the oxidation process, was based on mass balance between the inlets (Q_{IN} and Q_{OX}, **Fig. 3**) and the outlets (Q_{OUT} and Q_{OX}, **Fig. 3**) of the MBR. The capacity of the coupled MBR was defined as the volume of the MBR alone (V_{MBR}), leading to the following equation:

$$Q_{IN} \cdot C_{IN} + Q_{OX} \cdot C_{OXout} = Q_{OX} \cdot C_{OXin} + (Q_S + Q_{OUT}) \cdot C_{OUT} + r_{MBRCoupled} \cdot V_{MBR} \cdot C_{TSS} \qquad eq.9$$

Then:

$$r_{MBRCoupled} = \frac{Q_{IN} \cdot C_{IN} + Q_{OX} \cdot C_{OXout} - Q_{OX} \cdot C_{OXin} - (Q_{OUT} + Q_S) \cdot C_{OUT}}{V_{MBR} \cdot C_{TSS}} \qquad eq.10$$

and:

$$r_{MBRCoupled} = \frac{Q_{IN} \cdot (C_{IN} + C_{OXout} - 2 * C_{OUT})}{V_{MBR} \cdot C_{TSS}} \qquad eq.11$$

Table 2: Efficiency and removal rates of both pharmaceuticals for the different systems.

	Compound	MBR alone	MBR coupled	MBR+OX
Efficiency (%)	***CBZ***	*2.7 ± 28.7*	*58.9 ± 6.6*	*28.3 ±11.5*
	IBU	*97.9 ± 1.3*	*89.5 ± 12.7*	*87.2 ± 15.5*
Specific rate ($\mu g.g_{TSS}^{-1}.d^{-1}$)	**CBZ**	0.01 ± 0.12	0.13 ± 0.05	0.11 ± 0.01
	IBU	3.11 ± 0.04	3.01 ± 0.49	2.57 ± 0.46

Table 2 reports the removal efficiencies and specific rates for both IBU and CBZ in the three configurations, i.e. MBR alone (MBR), MBR alone in the coupling system (MBR Coupled), and the global coupled system (MBR+OX).

For IBU, the specific degradation rate of the MBR in the coupled process is not vastly different from the specific degradation rate of the MBR alone or the global coupled system. As stated previously, IBU is already highly biodegradable and so the photooxidation process did not significantly improve IBU removal. For CBZ, specific degradation rate went from 0.01 ± 0.12 $\mu g.g_{TSS}^{-1}.d^{-1}$ for the MBR alone to 0.13 ± 0.05 $\mu g.g_{TSS}^{-1}.d^{-1}$ for the MBR in the coupled system ($MBR_{Coupled}$) (**Table 2**). This finding shows that MBR performance on degrading CBZ was improved by the insertion of the oxidation process. Plugging the oxidation process into the MBR thus appears to intensify the degradation capacity selectively towards refractory molecules. Thus, while the ratio of degradation rates between IBU and CBZ was 300 for MBR alone, it tended towards 30 when the two processes were coupled (**Table 2**).

Let's address the relevance of this type of coupling (a configuration with recirculation in the photoreactor) compared to an association in series either in pre-treatment or post-treatment. The value of the oxidation process is that it can degrade refractory compounds, knowing that biodegradable carbonaceous compounds are currently perfectly well managed by biological processes. The results reported in **Table 2** show that IBU, which is a readily biodegradable compound, was almost totally degraded under the conditions set by the biological process (degradation rate remained stable whatever the MBR configuration: alone or coupled). The oxidation process therefore had a secondary role, neither improving nor disrupting the degradation of IBU. For CBZ, specific degradation rate was very sensitive to configuration. These results reflect the fact that this association intensified the degradation of the refractory compound. In a way, as the rate of IBU degradation was stable, the oxidation process acted selectively by privileging the degradation of CBZ. This behavior is assignable to the configuration that consisted in plugging the photoreactor in recirculation mode on the MBR. Indeed, by allowing the effluent and thus the compounds to circulate within the system, each process acted in a complementary way by playing its specific function. The MBR largely degraded the biodegradable compounds, leaving a minority to flow into the oxidation process, whereas the refractory compounds passing through the MBR flowed into the oxidation process. The selection induced between refractory and biodegradable compounds modifies the composition of the effluent, which was artificially concentrated in refractory compounds.

In the literature, associations in-series have proven effective, enabling high degradation rates. On the one hand, these associations can be costly and require the development of over-scaled oxidation processes that need to operate under the same conditions as the MBR (flow rate, residence time, TSS management).

On the other hand, the main but rare results obtained on coupled systems (in continuous mode) show high degradation rates on global performance indicators such as COD, BOD, and toxicity. However, these associations do not promote the degradation of the refractory compounds targeted under EU regulations [2]. They deliver a non-selective 'all-round' degradation of pollutant load that makes them under-efficient for the target substances, i.e. cost increase, oversizing, and overestimated operating conditions. The system proposed here works differently by proposing to exploit on the advantages of each of the two processes involved. By recirculating the effluent within the two processes, the system intensifies the capacities of each process by selecting the compounds requiring further treatment.

For future tests, this configuration will enable analysts to dissociate the roles on feed and recirculation flows, which is not possible with in-series configurations. For example, if the recirculation flow rate (Q_{OX}) is increased while keeping the residence time identical within each process (Q_{IN} = constant, V_{MBR} and V_{OX} constant), the number of times the effluent passes through the oxidation process will increases proportionally to this flow rate (Q_{OX}): by applying $Q_{OX} = n \cdot Q_{IN}$. It is anticipated that these operating conditions could be favorable to transform the compounds into by-products that may potentially become more biodegradable than the native molecules.

4. Conclusion

An innovative continuous process coupling a membrane bioreactor and a photoreactor is proposed for the removal of two pharmaceuticals (ibuprofen and carbamazepine) from wastewater. Implementing the photooxidation process in a recirculation loop on the membrane bioreactor had no negative impact on the removal efficiency of carbon, nitrogen and phosphorus pollution. No negative impact on the removal efficiency of biodegradable compounds such as ibuprofen was found, while at the same time a 10-fold improvement in the removal efficiency of biorecalcitrant compounds such as carbamazepine occurred. Furthermore, these results were achieved with a very low flux density of just 4 $W.m^{-2}$.

The interest and potential of this configuration coupling a photoreactor to the recirculation loop of the bioreactor have been discussed. The results reveal the relevance of this association which must be studied and optimized in order to intensify the performance of the system. The purpose is to get rid of the constraints imposed by the series configuration, by proposing to partially treat the micro pollutants during their passage in the oxidation process. Then, the by-products of the oxidized pollutants can be biodegraded by the membrane bioreactor. In this sense and contrary to the associations of reactors in series, this configuration makes it possible to play on the respective

residence times of two reactors, by varying the volumes of the reactors, but especially, the number of passages in the photo-reactor, by modulating the recirculation flow. These conditions should make it possible to intensify the performance of the coupling and in particular to accentuate the elimination of the by-products resulting from the degradation of the parent substances. In the long term, the bioreactor should also be associated with a solar photoreactor in order to take into account the effects of discontinuities in the solar resource (day/night cycle, cloudy periods) on the treatment capacities of the photoreactor and consequently of the coupled system.

Acknowledgment

This work received European sponsorship via the FEDER funds under the “Interreg SUDOE” program (Innovec’eau SOE1/P1/F0173) as well as regional sponsorship (PHOTODEPOL, N°19015248). This work was supported by French “Investments for the future” ("Investissements d'Avenir") program managed by the National Agency for Research (ANR) under contract ANR-10-LABX-22-01 (labex SOLSTICE).

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