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Estudio técnico y cinético de la eliminación de contaminantes de preocupación emergente para la reutilización de aguas residuales urbanas con procesos combinados

Antonio Monteoliva García

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Technical and kinetic study on the removal of contaminants of emerging concern for urban wastewater reuse by using combined processes

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Autor:
Antonio Monteoliva García

Directores:
Dr. D. Jaime Martín Pascual
Dr. Dª. María del Mar Muñío Martínez

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"A la cima no se llega superando a los demás, sino superándonos a nosotros mismos"
Anónimo

ABSTRACT

The appearance of new contaminants of emerging concern (CECs) in urban wastewater as a result of the consumption habits of today's society is compromising the incoming strategies for regeneration and reuse of wastewater in the European Union and even worldwide.

This work focuses on the removal of CECs for urban wastewater reuse, through the use of advanced treatment technologies that adapt and complement the conventional activated sludge (CAS) process to degrade contaminants of emerging concern in actual wastewater treatment plants (WWTPs).

For this purpose, the capacity of removal of CECs by using advanced oxidation processes (AOP) and its combination with other technologies such as membrane bioreactors (MBR) and moving bed biofilm reactors (MBBR) in membrane-based integrated approaches (MBR-AOP and MBBR-MBR-AOP) was evaluated.

The use of photo-assisted AOP (25 mg/L of H_2O_2) as tertiary treatment in urban WWTPs had as a result the complete removal of concentrations of CECs (carbamazepine, ciprofloxacin and ibuprofen) similar to those that are currently being detected in urban wastewater (59.83 μg/L, 22.30 μg/L and 54.60 μg/L respectively). However, a complete removal of CECs was not possible when their concentration in the water was higher, achieving yields

between 35.23 and 98.69 % for carbamazepine, between 93.45 and 100 % for ciprofloxacin and between 48.00 and 98.99 % for ibuprofen, depending on the treatment time (10-40 min), the peroxide dosage (25-100 mg/L) and the presence of catalysts (Fe^{+3} or TiO_2). Therefore, due to the more than possible increase in the concentration of these types of contaminants in urban wastewater in the coming years, part of the efforts to remove a greater amount of CECs from wastewater should be directed towards the improvement of the removal efficiency of the biological treatment.

In this sense, the removal of CECs in an MBR-AOP integrated approach was evaluated in a second experiment. The biological treatment, consisted on an MBR working at 16 h of hydraulic retention time and 4250 mg/L of mixed liquor suspended solids, was able to remove 66.23 % of carbamazepine, 100 % of ciprofloxacin and 90.04 % of ibuprofen from a wastewater containing 100, 10 and 100 μg/L of these contaminants respectively. Once the pollutant load in the biological treatment was significantly reduced, only 10 minutes of AOP treatment with 25 mg/L of hydrogen peroxide were sufficient to obtain reclaimed wastewater exempt of CECs.

Interestingly, a third experiment showed that the bioreactor combining both suspended and attached biomass (MBBR-MBR) proved to be a more robust and efficient treatment for urban wastewater regeneration. Although both treatments MBR and MBBR-MBR have a great potential to produce high quality reclaimed water according to proposal of directive

2018/0169/COD of urban wastewater reuse (BOD_5 < 10 mgO_2/L, suspended solids < 10 mg/L, turbidity < 5 NTU and E. coli < 10 CFU), the addition of carriers in the MBR (MBBR-MBR) led to a higher biodegradation capacity of CECs compared with the MBR, which increases the removal yields of CECs in the biological treatment (an increase of 9.02 % for carbamazepine and 5.30 % for ciprofloxacin, ibuprofen was completally removed in both experiments). Therefore, the addition of carriers in the MBR makes it possible to reduce the aggressiveness in the subsequent treatment by AOP. Concretely, a 5 min AOP treatment with 25 mg/L of hydrogen peroxide was sufficient to completely remove CECs from the reclaimed water. Furthermore, the MBBR-MBR-AOP configuration also presented a higher stability in the biological treatment compared with the MBR-AOP configuration due to the fact that the biomass is more safeguarded. While the MBBR-MBR system did not suffer alterations at the macroscopic level due to the sudden appearance of CECs in the wastewater, the presence of CECs in the wastewater caused a temporary instability in the MBR system, which suffered an important loss of biomass (the MLVSS decreased from 5233.45 to 4451.92 mg/L).

In conclusion, the results of this investigation confirmed that the combined use of membrane-based technologies with AOP has a high potential to remove CECs from wastewater and produce high quality reclaimed water in urban WWTPs, in accordance with the proposal of directive on the reuse of wastewater in the European Union.

RESUMEN

La aparición de nuevos contaminantes de preocupación emergente (CECs) en las aguas residuales urbanas como consecuencia de los hábitos de consumo de la sociedad actual está comprometiendo las futuras estrategias de regeneración y reutilización de las aguas residuales en la Unión Europea e incluso a nivel mundial.

Este trabajo se centra en la eliminación de CECs para la reutilización de las aguas residuales urbanas, mediante el uso de tecnologías de tratamiento avanzadas que se adapten al proceso de fangos activos convencional y lo complementen en la eliminación de CECs en las estaciones depuradoras de aguas residuales (EDARs) existentes. Para ello, se evaluó la capacidad de eliminación de CECs mediante el uso de procesos de oxidación avanzada (AOP) y su combinación con otras tecnologías tales como biorreactores de membrana (MBR) y reactores biológicos de lecho móvil (MBBR) en enfoques integrados basados en el uso de membranas (MBR-AOP and MBBR-MBR-AOP).

El uso de AOP foto-asistidos (25 mg/L of H_2O_2) como tratamiento terciario en EDARs urbanas tuvo como resultado la completa eliminación de concentraciones de CECs (carbamacepina, ciprofloxacina e ibuprofeno) similares a las que son detectados actualmente en aguas residuales urbanas (59.83 μg/L, 22.30 μg/L and 54.60 μg/L respectivamente). Sin embargo, no

fue posible la completa eliminación de CECs cuando la concentración de éstos en el agua era más alta, lográndose rendimientosentre el 35.23 y 98.69 % para la carbamacepina, entre el 93.45 y 100 % para la ciprofloxacina y entre el 48.00 y 98.99 % para el ibuprofeno, dependiendo del tiempo de tratamiento (10-40 min), la dosis de H_2O_2 (25-100 mg/L) y la presencia de catalizadores (Fe^{+3} o TiO_2). Por tanto, debido al más que posible aumento de la concentración de este tipo de contaminantes en el agua residual urbana en los próximos años, parte de los esfuerzos para eliminar una mayor cantidad de CECs del agua residual deben dirigirse hacia la mejora del rendimiento de eliminación en el tratamiento biológico.

En este sentido, en un segundo experimento se evaluó la eliminación de CECs en un enfoque integrado MBR-AOP. El tratamiento biológico, compuesto por un MBR trabajando a 16 h de tiempo de retención hidráulico y 4250 mg/L de sólidos en suspensión en el licor mezcla, fue capaz de eliminar un 66.23 % de carbamacepina, un 100 % de ciprofloxacina y un 90.04 % de ibuprofeno de un agua residual urbana que contenía 100, 10 y 100 μg/L of de estos contaminantes respectivamente. Una vez reducida notablemente la carga contaminante en el tratamiento biológico, sólo 10 minutos de tratamiento AOP con 25 mg/L de H_2O_2 fueron suficiente para obtener un agua regenerada libre de CECs.

Interesantemente, en un tercer experimento se demostró que el bioreactor combinando ambos tipo de biomasa, suspendida y fija, (MBBR-MBR) mostró ser un tratamiento más robusto y eficiente en la regeneración

del agua residual urbana. A pesar de que ambos tratamientos MBR and MBBR-MBR tienen un alto potencial para producir agua regenerada de alta calidad de acuerdo con la propuesta de directiva 2018/0169/COD de reutilización de aguas residuales urbanas (BOD_5 < 10 mgO_2/L, sólidos en suspensión < 10 mg/L, turbidez < 5 NTU and E. Coli < 10 CFU), la adición de soportes en un MBR (MBBR-MBR) conduce a una mayor capacidad de biodegradación de CECs frente al MBR, lo que aumenta los rendimientos de eliminación de CECs en el tratamiento biológico (incrementos del 9.02 % para la carbamacepina y 5.30 % para la ciprofloxacina y completa eliminación del ibuprofeno). Por tanto, la adición de soportes en el MBR permite reducir la agresividad en el tratamiento posterior por AOP. Concretamente, un tratamiento de 5 min por AOP con 25 mg/L de H_2O_2 fue suficiente para eliminar completamente los CECs del agua regenerada. Además, la configuración MBBR-MBR-AOP también presentó una mayor estabilidad del sistema biológico frente a la configuración MBR-AOP debido a que la biomasa, en forma de biopelícula, se encuentra más protegida. Mientras que el sistema MBBR-MBR no sufrió alteraciones a nivel macroscópico ante la aparición repentina de CECs en el agua residual, la presencia de CECs en el agua residual provocó una inestabilidad temporal en el sistema MBR, el cual sufrió una importante pérdida de biomasa (los sólidos en suspensión volátiles en el licor mezcla disminuyeron desde 5233.45 hasta 4451.92 mg/L).

En conclusión, los resultados de esta investigación confirmaron que el uso combinado de tecnologías basadas en el uso de membranas con AOP

tiene un alto potencial para eliminar CECs del agua residual y producir agua regenerada de alta calidad en EDARs urbanas, de acuerdo con la propuesta de directiva de reutilización de aguas residuales en la Unión Europea.

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1. Current situation and need for reuse

The growing demand for fresh water together with the degradation of receiving bodies as a consequence of wastewater discharges are causing the water resources available for human consumption to be increasingly scarce and of poorer quality (Ganiyu et al., 2015). This is the main consequence of the current linear economic model implemented in our society, based on "take, use and dispose" of natural resources (European Commision, 2015).

This alarming fact has led in recent years to the need for sustainable water management planning to protect the world's water resources. For this reason, in the coming years we will witness an inexorable transition from the current linear economic model to a circular economy model, whose premise is closing the loop (European Commission, 2016; Connor et al., 2017).

This paradigm shift requires to come over conventional wastewater management practices and adopt innovative approaches. In this sense, the reclamation of wastewater for subsequent reuse instead of discharge becomes the essential building block for achieving the paradigm shift, since it not only stops contributing to the degradation of receiving bodies by

avoiding discharge, but also provides an important source of water supply, thereby reducing the demand for natural water resources (European Commision, 2015). Indeed, some countries such as Spain have had their own wastewater reuse regulations in place for years to combat water scarcity. In the concrete case of Spanish RD 1620/2007, it establishes the requirements that treated wastewaters must meet according to their application (Table 1).

Table 1. Requirements for wastewater reuse in Spain.

Reclaimed water quality class			Main requirements			
			Nematodes (eggs/10L)	E. Coli (cfu/100mL)	TSS (mg/L)	Turbidity (NTU)
Quality 1. Urban applications	Quality 1.1.	Irrigation of private gardens; flushing of sanitary appliances.	≤ 1	0	≤ 10	≤ 2
	Quality 1.2.	Irrigation of urban green areas; street sweeping; fire-fighting system; industrial vehicle washing.	≤ 1	≤ 200	≤ 20	≤ 10
Quality 2. Agricultural applications	Quality 2.1.	Irrigation of crops with a water application system that allows direct contact of the reclaimed water with the edible parts for fresh human consumption.	≤ 1	≤ 100	≤ 20	≤ 10
	Quality 2.2.	Irrigation of products for human consumption with water application system that does not avoid direct contact of reclaimed water with edible parts, but consumption is not fresh but with subsequent industrial treatment; irrigation of pastures for consumption by dairy or meat producing animals; aquaculture.	≤ 1	≤ 1000	≤ 35	-
	Quality 2.3.	Localised irrigation of woody crops preventing contact of reclaimed water with fruits consumed for human consumption; irrigation of ornamental flower crops, nurseries, greenhouses without direct contact of reclaimed water	≤ 1	≤ 10000	≤ 35	-

		with crops; irrigation of non-food industrial crops, nurseries, silage fodder, cereals and oilseeds.				
Quality 3. Industrial applications	Quality 3.1a.	Process and cleaning water except in the food industry; other industrial uses.	-	≤ 10000	≤ 35	≤ 15
	Quality 3.1b.	Process and cleaning water in the food industry.	≤ 1	≤ 1000	≤ 35	-
	Quality 3.2.	Cooling towers and evaporative condensers.	≤ 1	0	≤ 5	≤ 1
Quality 4. Recreational applications	Quality 4.1.	Irrigation of golf courses.	≤ 1	≤ 200	≤ 20	≤ 10
	Quality 4.2.	Ponds, bodies of water and ornamental flowing streams where public access to water is prevented.	-	≤ 10000	≤ 35	-
Quality 5. Environmental uses	Quality 5.1.	Recharge of aquifers by localised percolation through the ground.	-	≤ 1000	≤ 35	-
	Quality 5.2.	Aquifer recharge by direct injection.	≤ 1	0	≤ 10	≤ 2
	Quality 5.3.	Irrigation of forests, green areas, and other areas not accessible to the public; forestry.	-	-	≤ 35	-
	Quality 5.4.	Other environmental uses (wetland maintenance, minimum flows and similar).	The minimum quality required will be considered for each case.			

Taking as an example the Spanish regulations among others, the European Commission has recently drawn up in the same line the proposal 2018/0169/COD whose objective is to establish the legal regime for the reuse of treated wastewater in the European Union (European Commission, 2018). This regulation aims to promote the improvement of the quality of treated wastewater in WWTPs for the use in agricultural irrigation, an activity that consumes 70% of freshwater withdrawals all over the world (Connor et al., 2017).

It lays down the minimum quality requirements that reclaimed water must meet to ensure sufficient protection of the environment and human health depending on the type of crop for which it is intended (European Commission, 2018b). As can be observed in Table 2, the physico-chemical quality requirements range from the minimums laid down in Directive 91/271/EEC on urban wastewater treatment (European Commission, 1991), to the stringent requirements laid down for the irrigation of food crops where the edible part is in direct contact with the reclaimed water (BOD_5 < 10 mgO_2/L, TSS < 10 mg/L and turbidity < 5 NTU). In addition, the Table 2 also shows the need for a disinfection process that achieves the microbiological quality requirements regarding the presence of fecal coliform bacteria.

Table 2. Requirements of water according to quality class.

Reclaimed water quality class			Requirements				
			Indicative technology target	E. Coli (cfu/100mL)	BOD5 (mg/L)	TSS (mg/L)	Turbidity (NTU)
A	All food crops, including root crops consumed raw and food crops where the edible part is in direct contact with reclaimed water	All irrigation methods	Secondary treatment, filtration, and disinfection	≤ 10	≤ 10	≤ 10	≤ 5
B	Food crops consumed raw where the edible part is produced above ground and is not in direct contact with reclaimed water, processed food crops	All irrigation methods	Secondary treatment, and disinfection	≤ 100	According to Directive 91/271/EEC (Annex I, Table 1)	According to Directive 91/271/EEC (Annex I, Table 1)	-
C		Drip irrigation* only	Secondary treatment, and disinfection	≤ 1000			-

	and non-food crops including crops to feed milk- or meat-producing animals						
D	Industrial, energy, and seeded crops	All irrigation methods	Secondary treatment, and disinfection	≤ 10000			-

2. Contaminants of emerging concern

Since the construction of wastewater treatment plants began in the 19th century, society's consumption habits have changed considerably, and therefore the pollutants discharged to wastewater (Yang et al., 2017).

This has led to the presence of new contaminants in urban wastewater not submitted to regulation, including substances such as pharmaceuticals, personal care products, industrial additives or pesticides (Alvarino et al., 2018). This fact has triggered a worldwide social alarm that threatens to endanger the environment and the society's public health (Kumar and Pal, 2018), so these contaminants are commonly referred to as contaminants of emerging concern (CECs). Although the concentration levels are still low (between ng/L and μg/L), they have already proven to have serious public health and/or environmental consequences (Gallardo-Altamirano et al., 2018). For example, small concentrations of pharmaceuticals have been observed in lettuce buds or edible tomatoes, also the presence of endocrine disruptors in drinking water, or most alarmingly, the development of antibiotic-resistant microorganisms as a consequence of the exposure to low

concentration of antibiotics in urban WWTPs (Chen et al., 2006; Sun et al., 2016; Fernandes et al., 2018).

Although there are no maximum discharge concentrations for CECs in the European Union, those that represent a potential risk are included in a watch list of substances (Decision 2018/840/EU) for which Union-wide monitoring data as concentrations, potential risks, etc. are to be gathered (European Commission, 2018c). After an evaluation of the data collected over 3 years, the list is updated, and those substances found to pose a significant risk will be reclassified as priority substances subject to regulation.

Furthermore, given the potential dangerousness that the presence of these pollutants in reclaimed water also represents, the proposal 2018/0169/COD also leaves open the possibility of including additional restrictions on the presence of CECs, with particular attention to pharmaceuticals and pesticides, with the aim of ensuring the safety of reclaimed water (European Commission, 2018b).

3. Wastewater resource recovery facilities (WRRFs): the new WWTPs

Traditionally, wastewater treatment plants were designed with the main objective of degrading the pollutants present in the wastewater in order to discharge it in appropriate conditions to reduce the impact on the environment as much as possible (Pal et al., 2014). For this purpose,

conventional WWTPs take advantage of biological processes, based on the metabolic activity of certain microorganisms contained in the urban wastewater, in a process widely known as conventional activated sludge (CAS).

However, after more than a century of operation, the treatment needs have changed, and such technology is beginning to be outdated, so the treatment technology of the WWTPs must be updated to adapt to the new requirements. And the current requirements are those related to reuse as a new source of water resources in a more circular economy; among others, the improvement of the quality of the treated water and the removal of new potentially harmful contaminants that may put wastewater reuse at risk (Ortiz Uribe et al., 2015).

For this reason, in the next few years the world is going to witness a radical change in the field of wastewater treatment, where conventional WWTPs, understood as facilities that generate waste and consume energy, are gradually going to give way to new wastewater resource recovery facilities (WRRFs), understood as facilities with more robust and efficient treatments, capable of producing directly reusable water and taking advantage of the energy produced in biological processes to be energy self-sufficient (Coats and Wilson, 2017).

Therefore, WRRFs are called to be the place where the change towards the new model of circular economy is forged, whose main activity will now

be the regeneration of wastewater for reuse, instead of its discharge as occurs in conventional WWTPs due to their linear conception (Ortiz Uribe et al., 2015).

But in order to carry out this change of paradigm, it is necessary to identify and evaluate new treatment technologies that are capable of adapting to the conventional purification method and complementing it to achieve a higher quality of the treated water: higher removal of organic matter, removal of CECs, removal of microorganisms from the water, etc.

4. Membrane bioreactor

The cornerstone of these WRRFs for wastewater reclamation could be the use of MBR technology, an improvement on the conventional activated sludge process in which the secondary clarifier is replaced by micro/ultrafiltration membranes (Gurung et al., 2016). This recent technology presents a series of technological and biological advantages with respect to the CAS process, among which it is worth highlighting a lower volume of treatment required, a higher concentration of microorganisms in the bioreactors, the development of slow-growing microorganisms due to a high sludge age, operational independence between the SRT and HRT or a reduction in sludge production and associated costs. This produces improvements in relation to the quality of the treated water compared to the

CAS process (Wijekoon et al., 2013; Gurung et al., 2016; Hamza et al., 2016; Martín-Pascual et al., 2016), such as:

- Higher organic matter removal (BOD_5 and COD) due to the higher biomass concentration in the mixed liquor.
- Improvement of the nitrification as a result of a higher SRT, which favours the growth of nitrifying bacteria.
- Complete removal of SS and an an effluent with less turbidity due to the replacement of the settling process by the filtration system.
- The disinfection of the treated wastewater is achieved as a result of the larger size of the microorganisms in relation to the pore diameter of the membranes.
- By removing the secondary clarifier, problems such as bulking are avoided, which considerably reduce the quality of the treated water.

Therefore, by using MBR technology, the water quality is improved with respect to the CAS process. On the other hand, the transformation of the CAS process into MBR could also considerably improve the removal of CECs due to the following advantages (Wijekoon et al., 2013; Hamza et al., 2016):

- The improvement of the biodegradation capacity of the system as a consequence of a higher MLSS concentration
- Removal of CECs adsorpted onto the sludge by separation by membranes

- The growth and development of specialized microorganisms that can degrade hardly biodegradable contaminants, as a result of increased SRT.

5. Moving bed biofilm reactor – membrane bioreactor

Moving bed technology is based on the growth and development of biomass as biofilm on the surface of plastic carriers that moves freely inside the bioreactor (Leyva-Díaz et al., 2017).

The growth of biomass in the form of biofilm allows the protection of microorganisms in a hostile environment, from which they selectively capture the substrates and nutrients needed to perform their vital functions (Litty et al., 2015). Within the biofilm different environments can coexist; while in the superficial layers of the biofilm nitrification and oxidation of organic matter take place under aerobic conditions, as one moves towards the innermost layers, oxygen deficit conditions begin to occur, in which the species present perform functions such as denitrification (Butler and Boltz, 2013).

The MBR systems can be easily combined with MBBR systems providing a hybrid technology called moving bed biofilm reactor - membrane bioreactor (MBBR-MBR) (Leyva-Díaz et al., 2014). In this form, the integration of a mobile bed with a MBR allows the coexistence of two types of biomass, one attached to the carriers and another in suspension. In

this way, the generation of aerobic and anoxic environments in the same reactor and the development of slow growing microorganisms are favoured. In this sense, the addition of carriers into the bioreactor could improve the performance of the MBR system (Litty et al., 2015):

- A higher robustness and stability of the biological system against toxic substances since the biomass is more safeguarded.
- A higher removal of CECs as a result of the simultaneous presence of aerobic and anoxic conditions and the presence of a higher biodiversity of microorganisms.
- The improvement of the quality of the treated water as a consequence of a higher concentration of microorganisms.

6. Advanced oxidation processes

One technology that is also called to form part of this new concept of WRRFs is the advanced oxidation processes (AOP). This treatment plays an important role in the regeneration of wastewater, as it ensures its disinfection and increases the removal performance of non-biodegraded CECs in the secondary treatment (Rizzo et al., 2019).

AOPs are based on a set of complex physical-chemical reactions for the generation of highly reactive species capable of oxidizing even the most persistent compounds (Fast et al., 2017). Among the different types of AOPs,

those based on the use of UV radiation have been positioned in recent years as a promising technology for the removal of CECs from urban wastewater.

In the case of photo-assisted H_2O_2/UV AOP, powerful and non-selective hydroxyl radicals are generated by the photochemical decomposition of hydrogen peroxide (Poyatos et al., 2010). The high oxidation potential of these radicals together with the UV light can achieve the total disinfection and degradation of non-biodegradable contaminants from the wastewater within minutes.

$$H_2O_2 \xrightarrow{hv} 2OH^{\bullet}$$

For contaminants with high chemical stability, it is possible to increase the rate of degradation by adding recoverable catalysts to the process. It has been shown that the addition of small dosages of ferrous salts (Fe^{+2}/H_2O_2/UV AOP) or semiconductor oxides (TiO_2/H_2O_2/UV AOP) can increase the generation of hydroxyl radicals in the water (Salimi et al., 2017).

The Photo-Fenton process (Fe^{+2}/H_2O_2/UV AOP) is based on a catalytic cycle in which hydroxyl radicals are continuously generated by oxidation of Fe^{+2} and photoreduction of the Fe^{+3} (Poyatos et al., 2010):

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^{\bullet}$$

$$Fe^{+3} + H_2O \xrightarrow{hv} Fe^{+2} + H^+ + OH^{\bullet}$$

$$H_2O_2 \xrightarrow{hv} 2OH^{\bullet}$$

On the other hand, Heterogeneous Photocatalysis (TiO_2/H_2O_2/UV AOP) is based on the continuous generation of hydroxyl radicals due to a charge separation on the surface of the TiO_2 particles caused by the incidence of the UV light (Poyatos et al., 2010):

$$TiO_2 \overset{h\nu}{\rightarrow} TiO_2(e^- + h^+)$$
$$TiO_2h^+ + OH^- \rightarrow TiO_2 + OH^\bullet$$
$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^-$$

7. Integrated approaches

Given the imperative necessity to generate quality water resources based on urban wastewater regeneration in WWTPs, the use of integrated approaches that combine physicochemical and biological treatment processes becomes mandatory in the incoming years.

The combined use of advanced treatments could produce positive synergies in the quality of the reclaimed water. A positive synergy could be expected as membrane-based bioreactors generate ultra-filtered effluents with high transmittance, ideal for AOPs where the energy source is UV light. By this way, MBR-AOP combined treatments could have a great potential to produce high quality reclaimed water.

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II - OBJECTIVES

II - OBJECTIVES

This work aimed to assess the removal of CECs from urban wastewater by using advanced processes or a combination of them, with the final purpose of promoting urban wastewater reuse practices.

To this end, a series of secondary objectives have been proposed to be achieved for the correct completion of the doctoral thesis:

- To evaluate the removal mechanism and the removal capacity of carbamazepine, ciprofloxacin and ibuprofen by using three different AOP: H_2O_2/UV, Fe^{+3}/H_2O_2/UV and TiO_2/H_2O_2/UV.
- To evaluate the removal mechanism and the removal capacity of carbamazepine, ciprofloxacin and ibuprofen by using MBR.
- To evaluate the removal capacity of carbamazepine, ciprofloxacin and ibuprofen by using the combined treatment technology MBR-AOP.
- To evaluate the quality of reclaimed wastewater by the combined treatment technology MBR-AOP according to parameters from proposal 2018/0169/COD for wastewater reuse, i.e, BOD_5, TSS, turbidity and E. Coli.
- To evaluate the effects of the incorporation of carriers in the biological system of the combined treatment technology MBR-

AOP, relative to: a) carbamazepine, ciprofloxacin and ibuprofen removal; b) reclaimed wastewater quality according to parameters of proposal 2018/0169/COD, i.e., BOD_5, TSS, turbidity and E. Coli; and c) stability of the biological process.

III - METHODOLOGY

III - METHODOLOGY

1. Experimental set-up

In order to achieve the objectives established in the thesis, three different advanced treatment technologies were evaluated in order to produce high-quality reclaimed water, i.e. MBR, MBBR and AOP. The experimental device used was composed of two reactors: a biological reactor and a photochemical reactor.

In the biological reactor, henceforth bioreactor, the biological treatment of the urban wastewater was performed by using a membrane-based technology. Depending on the technology to be evaluated, the bioreactor could operate as MBR or MBBR-MBR (Figure 1). The body of the bioreactor was composed of two tanks of different capacity and shape. On the one hand, a cylindrical tank of 272 L capacity, divided into an anoxic zone where the denitrification and degradation processes of part of the organic matter took place, and a larger aerobic zone where the nitrification was carried out and the degradation of the organic matter was completed. The necessary oxygen was supplied by an air compressor and a fine bubble diffuser. The bioreactor had an automated system to maintain the DO in the aerobic zone around a previously established set point. On the other hand, a rectangular tank of 78 L capacity where the separation of the treated water from the

mixed liquor was carried out by means of 4 hollow-fiber membranes. A blower continuously supplied air to the rectangular tank for air scouring the membranes. The bioreactor also included three water pumps: a feed pump that continuously supplied urban wastewater to the bioreactor; an internal recycling pump to keep the concentration of MLSS in both tanks homogeneous; and a permeate pump that operated in cycles of 10 minutes, 9 minutes and 35 seconds filtering and 25 seconds backwashing the membranes with ultrafiltered water.

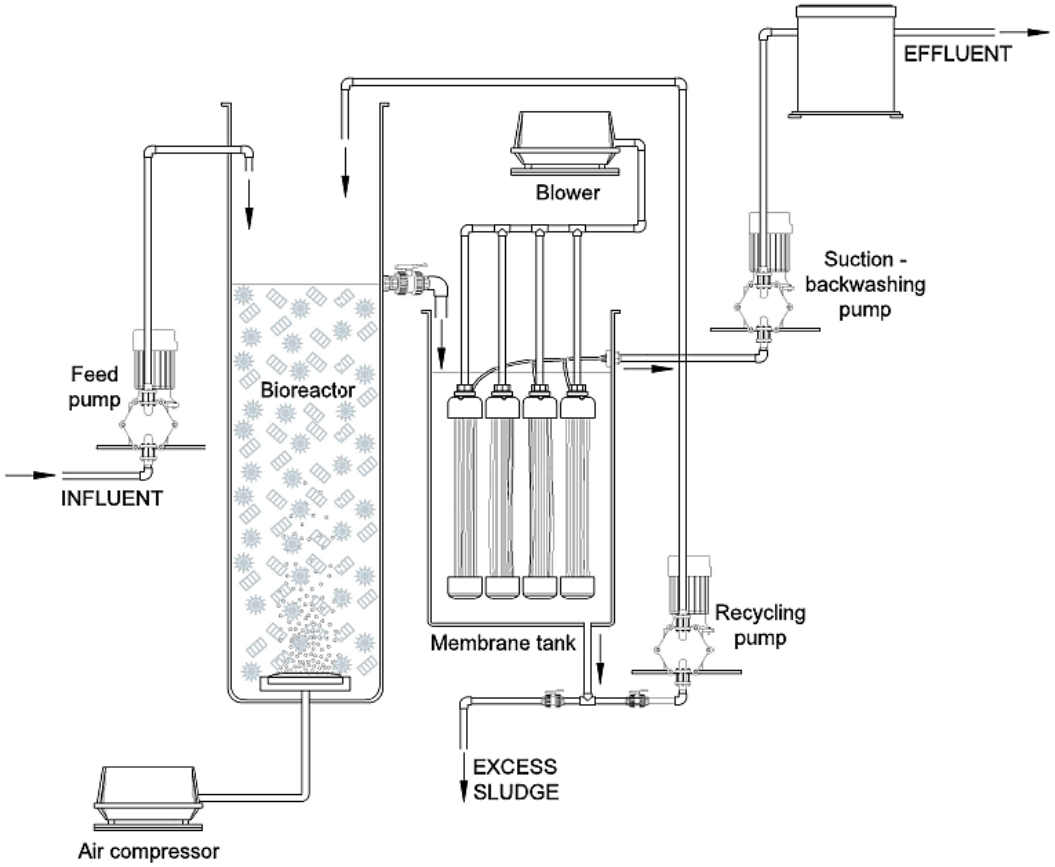

Figure 1. Biological reactor used in the experiments.

In the photochemical reactor, henceforth photoreactor, the physicochemical treatment of the urban wastewater was carried out by AOP technology (Figure 2). It consisted on a highly efficient lab-scale reactor for photochemically catalyzed reactions (UV-Consulting Pesch®). The photoreactor is a cylindrical vessel made of quartz with a net reaction volume of 0.8 L. A medium-pressure mercury vapour lamp with a broad emission spectrum in the UV range above 190 nm (UV emitter TQ150®) is placed in an immersion tube in the central axis of the reactor to achieve an optimal distribution of the emitted photons. The lamp is also isolated from the reaction medium by means of a cooling jacket that dissipates the heat generated by the emitter and cools it down to the reaction temperature. The perfect mixing condition inside the reactor is achieved by a magnetic stirrer emplaced under the reactor.

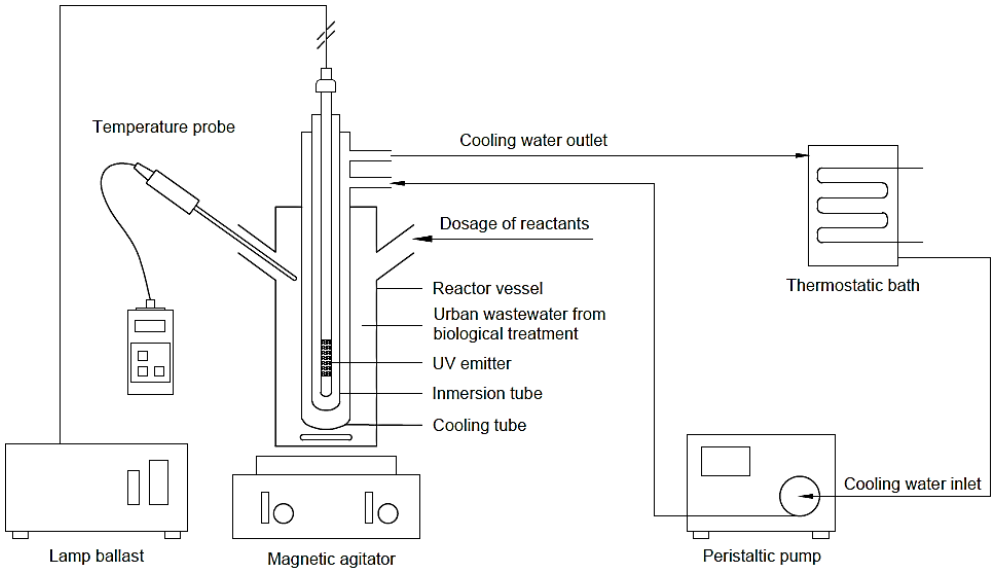

Figure 2. Batch photochemical reactor used in the experiments.

2. Description of the experimental procedure

Three different treatments for urban wastewater regeneration were evaluated by conducting three different studies: the use of AOP as tertiary treatment in conventional WWTPs, and two combined approaches: MBR-AOP and MBBR-MBR-AOP.

The first one focused on the removal of CECs from urban wastewater by using AOP technology as tertiary treatment in WWTPs. For this purpose, three solutions of carbamazepine, ciprofloxacin and ibuprofen in increasing concentrations were prepared in a matrix of real urban wastewater effluent from WWTP Granada Oeste and treated by AOP in the photoreactor. The first solution consisted on urban wastewater containing 59.83 μg/L of carbamazepine, 22.30 μg/L of ciprofloxacin and 54.60 μg/L of ibuprofen. The second solution of urban wastewater contained 95.03 μg/L of carbamazepine, 17.17 μg/L of ciprofloxacin and 69.60 μg/L of ibuprofen. While the third solution contained concentrations of 281.00, 98.53 and 275.00 μg/L of carbamazepine, ciprofloxacin and ibuprofen, respectively.

Each of the three wastewater samples was summited to 9 different assays, in a combination of different dosages of hydrogen peroxide and catalysts (Table 3). All the tests were carried out at 20 °C and without modifying the pH of the wastewater (6.67), since modifying the pH of large volumes of wastewater is not economically feasible, since it is a buffered

medium as a result of the concentrations of CO_3/HCO_3 present in the wastewater.

Table 3. AOP assays for wastewater samples in the first study.

Assay	Peroxide dosage (mg/L)	Fe^{+2} catalyst dosage (mg/L)	TiO_2 catalyst dosage (mg/L)
1	25	-	-
2	50	-	-
3	100	-	-
4	25	40	-
5	50	40	-
6	100	40	-
7	25	-	1000
8	50	-	1000
9	100	-	1000

In the second study, the removal of higher concentrations of CECs in wastewater was evaluated using an MBR-AOP combined approach. The addition of membranes in the CAS process could improve the degradation of CECs in the secondary treatment, and thus the overall removal performance in WWTPs. In this way, the load of CECs to the photoreactor, and consequently the necessary treatment time and reagent dosages, could be considerably reduced, which would allow to reduce the costs derived from a more aggressive treatment in the tertiary treatment.

For this purpose, a pilot-scale MBR emplaced in the WWTP Granada Oeste was treating continuously (16 h of HRT and 4250 mg/L of MLSS) real urban wastewater doped in order to simulate concentrations of 100, 10 and

100 μg/L of carbamazepine, ciprofloxacin and ibuprofen in the influent. Effluent samples were collected and subsequently treated in the photoreactor by AOP, using the optimum operating conditions obtained in the first study. Additionally, the concentration of CECs in the influent was progressively increased to 5000, 500 and 5000 μg/L of carbamazepine, ciprofloxacin and ibuprofen in order to evaluate the maximum CEC removal capacity of the combined treatment.

Finally, the third study evaluated the quality of the reclaimed water in the MBR-AOP combined treatment using as indicators the removal of CECs and those established in the European proposal 2018/0169/COD for reuse (European Commission, 2018), and compared it with that obtained by adding biological treatment carriers, in a configuration MBBR-MBR-AOP. It is possible that the joint presence of biomass in suspension and as biofilm in the bioreactor could increase the removal yield of CECs in the biological treatment and allow to decrease the reagent doses and therefore the operational costs in the AOP tertiary treatment. Other possible effects on reclaimed water quality and process stability were evaluated.

To this end, a first experiment was launched in which real urban wastewater containing 100 μg/L of carbamazepine, 10 μg /L of ciprofloxacin and 100 μg /L of ibuprofen was continuously treated in an MBR-AOP pilot scale working at 10 h of HRT, 6500 mg/L of MLSS and 25 mg/L of hydrogen peroxide dosage over 15 min. Once results were obtained, a second

experiment was launched, in which the pilot-scale was operated at the same conditions but with 35% of the bioreactor volume filled with AnoxKaldnes™ K1 carriers.

Table 4. Assays carried out in second and third studies.

Assay	Biological treatment			Physico-chemical treatment	
	Treatment	HRT (h)	MLSS (mg/L)	Treatment	H_2O_2 dosage (mg/L)
1	MBR	16	4250	H_2O_2/UV AOP	25, 50 and 100
2	MBR	10	6500	H_2O_2/UV AOP	25
3	MBR-MBBR (35% filling ratio)	10	6500	H_2O_2/UV AOP	25

3. Analytical determinations

3.1. Physicochemical determinations

The organic matter content in wastewater samples were measured as biological oxygen demand at fith day (BOD_5), chemical oxygen demand (COD) and total organic carbón (TOC). BOD_5 was analyzed by the manometric method according to APHA, which consists of the indirect measurement of the oxygen consumed by the bacteria present in the samples (APHA, 2012). The measure of COD was performed by a strong oxidation of the organic matter in a strong acid medium (excess of H_2SO_4), employing an oxidant such as potassium dichromate ($Cr_2O_7K_2$) and bringing the

reaction up to 150 ºC (APHA, 2012). TOC was determined indirectly by using a Formacs HT TOC/TN Analyzer. The measure of the total carbon by the oxidation of the carbon present in the sample to CO_2 at 950 ºC in the presence of a cobalt catalyst is subsequently compared with the measure of the inorganic fraction determined by its oxidation to CO_2 employing H_3PO_4 (85% v/v). TOC was determined by the difference between both values.

The determination of Total Suspended Solids (TSS) was performed according to the gravimetric method from the APHA, based on the weight increase of a 0.45 μm filter after the vacuum filtration of a sample and its subsequent dryness to 105 ºC (APHA, 2012). The fraction of volatile suspended solids (VSS) is determined by the weight loss of the filter when exposed to 550 ºC for 20 minutes (APHA, 2012). To measure the SS concentration in the biofilm (BFSS), a sample of 10 carriers was added to a 50 mL Tween 80 surfactant dispersant solution and centrifuged for 20 min at 3000 rpm (Rodríguez-Sánchez et al., 2017). Subsequently, the solid residue was subjected to the APHA method for analysis of TSS and VSS (APHA, 2012).

Conductivity of samples was measured with a conductivity meter Crison CM 35®, while pH and temperature were measured with a pHmeter Crison pH 25®.

The turbidity was analyzed according to the nephelometric method from UNE-EN ISO 7027-1:2016 which measures the diffuse radiation of a

water sample based on the concentration of a Hydrazine Sulphate and Hexamethylenetetramine suspension in known proportions (UNE, 2016). By other hand, colour was measured according to method B from UNE-EN ISO 7887:2012, consisting of the determination of true colour by spectrophotometry at different wavelengths (UNE, 2012).

The recount of E. coli was carried out using the membrane filtration method according to Difco™ Manual, based on running the sample through a membrane filter and subsequent incubation at 44 °C in Petri dich with Endo Agar as culture medium (Zimbro and Power, 2003).

Toxicity was measured by means of the LUMIStox test in accordance with the UNE EN ISO 11348-2:2009 standard, based on the inhibition of the light intensity of the Vibrio fisheri strain marine bacteria that occurs after a certain exposure time of the bacteria with the wastewater sample (UNE, 2009).

The concentration of CECs in water and sludge samples was determined using high-performance liquid chromatography with a triple-quadrupole mass spectrometry detector. For this, an analytical method was developed in an Acquity UPLC System H-Class with Acquity UPLC BEH™ C18 column (2.1 x 150 mm, 1.7 μm). More details of the essays and validation of the method can be obtained in each Chapter.

3.2. Respirometric assays

Respirometry is a technique that analyzes the kinetic behavior of the microbial community from a bioreactor (Leyva-Díaz et al., 2014). It is based on the measurement of the oxygen consumption of the bacteria contained in an activated sludge, either for its maintenance (endogenous respiration) or for the degradation of an organic or nitrogen-ammonium substrate (exogenous respiration).

The respirometric experiments were carried out in a BM-Advance respirometer (SURCIS®). This equipment consists of a 1 L capacity reactor vessel placed in a Peltier-type thermostat which allows the tests to be carried out at a constant temperature. The reactor vessel is divided into two compartments that separate the air diffuser from the DO sensor, in order to avoid erroneous measurements due to the direct exposure of the sensor to the air flow. Therefore, the sensor DO is located in the lower compartment, while the air diffuser is located in the upper compartment. To link both compartments and keep the mixture homogeneous throughout the reactor, there is a recirculation of the activated sludge from the lower compartment to the upper compartment. Both compartments maintain perfect mixing conditions by means of an agitator located on the axial axis of the reactor vessel.

To carry out the tests, the collection of the activated sludge sample and its placement in aeration for a period between 12-18 h was mandatory in order to reach the endogenous phase (Leyva-Díaz et al., 2013).

Once the endogenous phase was reached, the dynamic test for heterotrophic bacteria was performed, based on the analysis of the exogenous respiration of the heterotrophic bacteria (Leyva-Díaz et al., 2013). This test serves to determine the maximum growth rate (μ_{max}), the Monod constant (K_M), the production rate (Y_H) and the rate of consumption of organic matter ($r_{su,H}$). For this purpose, 1 L of mixed liquor in endogenous phase, to which a concentration of Allylthiourea was previously added to inhibit the activity of the autotrophic bacteria, was introduced into the respirometer. Three samples of sodium acetate were added at different concentrations and the variation in DO is recorded.

After completion of the dynamic test and once the endogenous phase was recovered again, the static test for heterotrophic bacteria was performed, based on the analysis of the endogenous respiration of the heterotrophic bacteria. It serves to determine the rate of oxygen consumption by these bacteria. This test serves to determine the oxygen uptake rate (OUR) and the decay rate (b_H) of heterotrophic bacteria. To do this, the air supply in the bioreactor was stopped and the rate of oxygen consumption by the biomass was monitored, recording the DO values inside the reactor vessel (Leyva-Díaz et al., 2013).

4. Mass balances and reaction rates

4.1. Biological degradation rate

The removal efficiency of CECs from water in the biological treatment was calculated based on the results of the analyses on the influent and the effluent of the bioreactor. However, this value does not provide information on the actual biodegradation capacity of the particular system, as some of the CECs are not actually degraded by the biomass, but are adsorbed into the sludge and escape through the excess sludge, depending on molecular structures and functional groups of the CECs (Wijekoon et al., 2013).

Therefore, in order to assess the actual degradation capacity of CECs of the biological treatment in particular, excess sludge samples were also analysed and the biological degradation rate (BDR) was calculated by means of a mass balance to the system:

$$Q_{in} \cdot C_{in} = Q_{pe} \cdot C_{pe} + Q_w \cdot C_w + V \cdot \frac{dC_{BR}}{dt} + BDR \cdot X$$

Whereas the concentration of pharmaceuticals inside the bioreactor remained constant due to the continuous and controlled entry of pharmaceuticals into the reactor, the BDR can be obtained according to the equation:

$$BDR = \frac{1}{X} \cdot \left(Q_{in} \cdot C_{in} - Q_{pe} \cdot C_{pe} - Q_w \cdot C_w\right)$$

4.2. Phisicochemical degradation rate

In order to evaluate the degradation capacity of CECs by photo-assited AOP and to delve into the reaction mechanism that takes place in such treatment, the physicochemical degradation rate (PDR), represented below as k, was calculated from the adjustment to the kinetic model that best represents the experimental results.

$$-\frac{dC}{dt} = k \cdot C^n$$

The models evaluated were those commonly used to describe the mechanisms of reaction of elementary chemical reactions:

Kinetic model	Elementary equation	Developed equation
Zero order	$-\frac{dC}{dt} = k \cdot C^0$	$C = C_0 - k \cdot t$
First order	$-\frac{dC}{dt} = k \cdot C^1$	$C = C_0 \cdot e^{-k \cdot t}$
Second order	$-\frac{dC}{dt} = k \cdot C^2$	$C = \frac{C_0}{1 + C_0 \cdot k \cdot t}$
Third order	$-\frac{dC}{dt} = k \cdot C^3$	$C = \frac{C_0}{\sqrt{1 + 2 \cdot k \cdot t \cdot {C_0}^2}}$
Pseudo-first order	$-\frac{dC}{dt} = k \cdot (C_e - C)$	$C = C_0 \cdot e^{k \cdot t} + C_e \cdot \left(1 - e^{k \cdot t}\right)$
Pseudo-second order	$-\frac{dC}{dt} = k \cdot (C_e - C)^2$	$C = C_e + \frac{(C_0 - C_e)}{1 + k \cdot t \cdot (C_0 - C_e)}$

4.3. Kinetic characterization of the biomass

4.3.1. Yield coefficient for heterotrophic biomass ($Y_{H,VSS}$)

The yield coefficient for heterotrophic biomass ($Y_{H,VSS}$) is defined as the ratio between biomass growth per amount of substrate consumed (Leyva-Díaz et al., 2013).

$$Y = -\frac{\frac{dX}{dt}}{\frac{dS}{dt}}$$

Expressing its value in terms of oxygen consumption by means of the conversion factor f_{CV}=1.48 mg COD/mg VSS,

$$Y_{H,VSS} = \frac{Y_{H,O_2}}{f_{CV}}$$

can be determined from the oxygen consumption obtained in the dynamic test:

$$Y_{H,O_2} = \frac{S - OC}{S}$$

where:

$$OC = \int_{t_0}^{t} R_s \cdot dt$$

4.3.2. Substrate degradation rate ($r_{su,H}$)

The substrate degradation rate ($r_{su,H}$) can be expressed as the variation of the substrate concentration over time (Leyva-Díaz et al., 2013):

$$r_{su,H} = \frac{dS}{dt}$$

From Helle's equation seen above, the substrate can be expressed as a function of the oxygen consumed:

$$Y_{H,O_2} = \frac{S - OC}{S} \rightarrow S = \frac{OC}{1 - Y_{H,O_2}}$$

Therefore, the rate of degradation of organic matter by heterotrophic biomass can be calculated as follows:

$$r_{su,H} = \frac{dS}{dt} = \frac{1}{1 - Y_{H,O_2}} \cdot \frac{dOC}{dt} \rightarrow r_{su,H} = \frac{1}{1 - Y_{H,O_2}} \cdot \frac{d}{dt}\left(\int_{t_0}^{t} R_S \cdot dt \right) \rightarrow$$

$$r_{su,H} = \frac{R_S}{1 - Y_{H,O_2}}$$

4.3.3. Monod model constants: maximum growth rate (μ_m) and semisaturation constant (K_S)

Assuming that the growth rate of biomass (r_x) can be expressed as:

$$r_x = \mu \cdot X_H = Y_{H,VSS} \cdot r_{su,H}$$

The empirical growth rate can be found from respirometry tests (Leyva-Díaz et al., 2013):

$$\mu_{emp} = \frac{Y_{H,VSS} \cdot r_{su,H}}{X_H}$$

and therefore, the constants of the Monod model by the linearization of the model equation and the adjustment of rates μ_{emp} obtained for each evaluated substrate:

$$\mu = \mu_m \cdot \frac{S}{K_S + S} \quad \rightarrow \quad Linealization \quad \rightarrow \quad \frac{1}{\mu_{emp}} = \frac{K_S}{\mu_m} \cdot \frac{1}{S} + \frac{1}{\mu_m}$$

4.3.4. Endogenous respiration coefficient for heterotrophic biomass (b_H)

The endogenous respiration coefficient, also called decay coefficient, for heterotrophic biomass (b_H) can be determined from the total endogenous respiration coefficient (k_d) by analysis of the fraction of volatile biomass $(1 - f_p)$:

$$b_H = \frac{k_d}{1 - Y_{H,VSS} \cdot (1 - f_p)}$$

Since it is possible to determine k_d directly from the results of OUR_{end} obtained in the static test (Leyva-Díaz et al., 2013):

$$k_d = \frac{OUR_{endogena}}{1.42 \cdot X_T}$$

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IV - CHAPTER 1

Removal of carbamazepine, ciprofloxacin and ibuprofen in real urban wastewater by using light-driven advanced oxidation processes.

IV - CHAPTER 1

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1. Abstract

This study focuses on the use of advanced oxidation processes as a tertiary treatment in wastewater treatment plants to degrade contaminants of emerging concern at the natural pH of the biologically treated wastewater. Different peroxide dosages and initial concentrations of a mix of three pharmaceuticals commonly present in wastewater (carbamazepine, ciprofloxacin and ibuprofen) were tested in a batch photoreactor. The addition of Fe^{2+} and TiO_2 as catalysts was also tested with the aim of improving the degradation rate of the pharmaceuticals. Among the contaminants tested, ciprofloxacin was the pollutant that showed the best

degradation. It was completely removed from water after 20 min of treatment under any of the experimental conditions assessed. High degradation percentages, between 89.83 and 100%, were achieved for ibuprofen, while carbamazepine shows the lowest degradation, ranging from 80.14 to 100%. In terms of global efficiency, a complete degradation was achieved when the concentration of the tested contaminants was similar to current concentration levels in urban wastewater effluents. The addition of the catalysts did not significantly improve the degradation rates.

2. Introduction

It is widely known that water resources are being exploited in non-sustainable ways under the framework of linear economy of the contemporary European society, based on a "take, use and dispose" model (European Commission 2015).

Water is being subjected to an increasing pressure caused by the continuous growth of its demand and also by the degradation of water resources through the discharge of wastewaters (Ganiyu et al. 2015). Hence, under this economic approach, water resources are becoming increasingly scarce and are seeing their quality reduced.

In order to avoid the problem of scarcity of natural resources and to ensure its sustainability, a set of measures have been launched from the European Union (EU) to replace the current linear economy with a new model of a circular economy, based on the premise of "cradle to cradle" for

products, waste and resources, in such a way that the value of these is maintained in the economy for the longest time possible, reducing to the minimum the consumption of natural resources and the generation of waste (European Commision 2015). Among the adopted key measures that are going to be implemented within the mandate of the current Commission, there are a series of actions to enhance the reuse of wastewater at the European level (European Commission 2016). For this reason, the effective treatment of wastewater and its subsequent reuse are going to be the key tools in the coming years to face the increasingly restrictive regulations that seek to effectively close the water cycle in order to ensure its sustainability.

Originally, wastewater treatment plants (WWTPs) were designed to eliminate the main pollutants in water that numerous efforts have attempted to combat since the beginning from the scope of the EU's water policy, mainly including pollutants of greater presence in wastewater from urban areas: suspended solids and organic matter (Yang et al. 2017).

However, because of the consumption habits existing in the present-day society, numerous pollutants not submitted to regulation are beginning to be detected frequently in a multitude of wastewater discharges in concentrations ranging from ng/L to μg/L (Gallardo-Altamirano et al. 2018). These substances are commonly referred to as contaminants of emerging concern (CEC), given the possible consequences that may result from their presence in the water bodies of the planet (Sauvé and Desrosiers 2014). Among them, there have been found in wastewater some substances such as pharmaceuticals, personal care products, industrial additives, pesticides

and a wide range of chemical compounds (Alvarino et al. 2018). Over the past decade, many authors have been observing and writing in their research articles how the treatment technology of the current WWTPs, based on biological degradation, becomes inadequate when facing the new problematic of CEC, due to them mostly being recalcitrant substances or barely biodegradable (Rizzo et al. 2019).

Therefore, due to the inexistence nowadays of the proper technology for their effective removal in such facilities, the CECs end up by being discharged through the treated effluents. For this reason, both possible reuse and discharge to a natural body water become inadequate (Shu et al. 2016).

Considering the above, many researches are being carried out recently with the aim to identify and evaluate the efficiency of other alternative treatment technologies, capable of adapting to the wastewater treatment conventional method and complementing it in the removal of CEC, without considerably increasing the economic and energetic costs of the process (Rodriguez-Narvaez et al. 2017).

Since a large percentage of the CEC are recalcitrant substances, advanced oxidation processes (AOPs) are called to be the solution for the treatment of these contaminants because they are adequate alternatives to remove persistent contaminants when biological processes are not enough (Lopez–Lopez et al. 2015). Multiple effective approaches, such as ozonation (Rozas et al. 2017), ultraviolet light (UV) (Afonso-Olivares et al. 2016), photocatalysis (Hassani et al. 2015), Fenton process (Oliveira et al. 2014) and

combined ones (Soriano-Molina et al. 2019), have been suggested to degrade CECs from water.

The degradation of organic pollutants by using AOP is based on the generation of highly reactive species (Fast et al. 2017). In the case of photo-assisted H_2O_2/UV/AOP, hydroxyl radicals are generated by photochemical decomposition of hydrogen peroxide (Eq. 1) (Poyatos et al. 2010).

$$H_2O_2 \rightarrow hv \rightarrow 2OH^{\cdot} \quad (1)$$

These radicals have a high oxidation potential capable of degrading the CECs (Eq. 2),

$$CEC + OH^{\cdot} \rightarrow products \quad (2)$$

Whose theoretical degradation rate would be given by the second-order kinetic (Eq. 3).

$$v = -\frac{d[CEC]}{dt} = k \cdot [CEC] \cdot [OH^{\cdot}] \quad (3)$$

This degradation rate can be considerably improved by using catalysts. It has been proved that it is possible to increase the generation rate of hydroxyl radicals in the presence of ferrous salts (photo-Fenton) or semiconductor oxides (heterogeneous photocatalysis) (Salimi et al. 2017). Photo-Fenton AOP occurs when the Fenton's reagent Fe^{2+} becomes oxidized at acidic conditions in a H_2O_2/UV AOP, forming soluble aquo-Fe^{3+} complexes, which generates hydroxyl radicals. These complexes are then submitted to photoreduction, forming more hydroxyl radicals and the Fe^{2+} ion, indispensable in order to continue the photo-Fenton iron cycle

(Klamerth et al. 2013). In the case of the heterogeneous photocatalysis, based on the addition of semiconductor oxides (generally titanium dioxide) to the H_2O_2/UV AOP, the photons of a UV light source induce in the semiconductor a charge separation that can lead to the formation of hydroxyl radicals (Kaur et al. 2016).

The main purpose of the research was to analyze the results of applying a photo-assisted AOP as tertiary treatment for the removal of CEC from the effluent of the WWTPs before its reuse. This research was carried out in the laboratories of the University of Granada (Spain) during the months of May and June 2018. To achieve the goal of this research, real urban wastewater was spiked with a mix of three common CEC (carbamazepine, ciprofloxacin and ibuprofen) was treated by using photo-assisted H_2O_2/UV AOP at 20 °C without modifying the pH. The degradation efficiency of the mix was evaluated at different initial concentrations in the range of μg/L using different dosages of hydrogen peroxide (25, 50 and 100 mg/L). The addition of 40 mg/L Fe^{2+} (photo-Fenton process) and 1000 mg/L TiO_2 (heterogeneous photocatalysis) was also tested to analyze whether these catalysts could improve the total efficiency of the process to remove the pharmaceuticals. Kinetics of the process was modeled to obtain the degradation rates of the pollutants tested. Finally, the effect of the operative variables (initial concentration, peroxide dosage and catalyst addition) on the degradation efficiency of the process was studied.

3. Materials and methods

3.1. Experimental set-up

The AOP were carried out using a laboratory UV reactor system provided by the company UV-Consulting Peschl®, a highly efficient system for photochemically catalyzed reactions (Figure 3). This photochemical system is composed of a cylindrical quartz reactor vessel which possesses a net reaction volume of 700 mL. In its interior is placed a UV emitter TQ150 (150 W) with the help of a quartz glass immersion tube, which protects it against direct contact with the reaction medium and which provides a UV transmission level of 92%. The UV emitter is a medium-pressure mercury vapor lamp with a broad emission spectrum in the UV range above 190 nm. To dissipate the radiant heat produced by the UV lamp, a cooling jacket external to the immersion tube was used.

In order to homogenize the reaction medium, the photoreactor was placed on a magnetic stirrer. Since the walls of the reactor vessel are made of quartz, the photoreactor was covered with aluminum foil in order to avoid losing part of the radiation produced by the UV lamp by transmission, also avoiding interferences with radiations oblivious to the system.

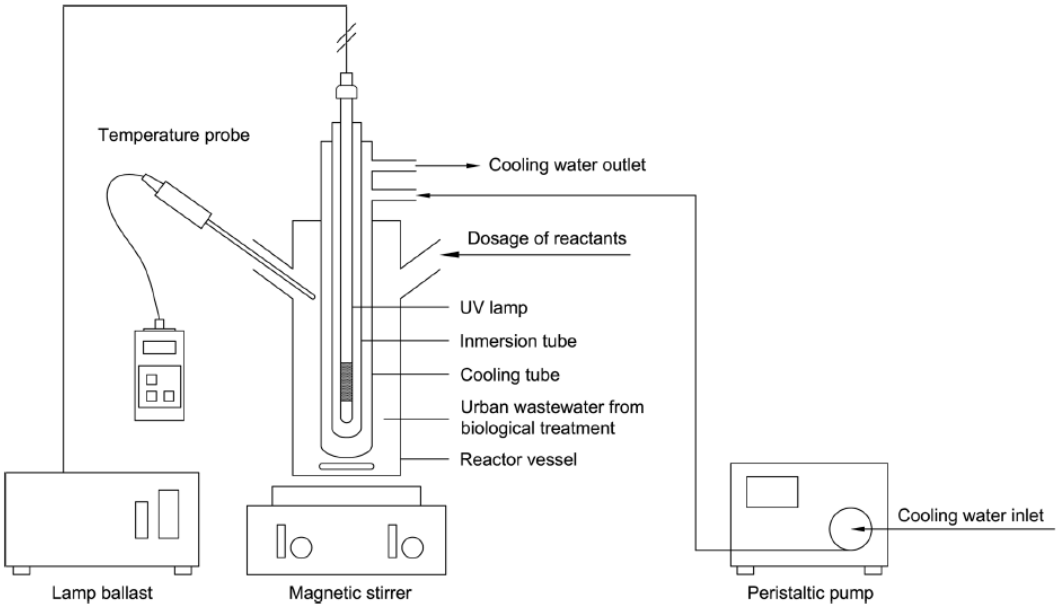

Figure 3. Experimental setup

3.2. Experimental procedure

To evaluate the degradation capacity of CEC from WWTPs effluents by using photo-assisted AOP, experiments were carried out with real urban wastewater from the effluent of the biological treatment in the WWTP Granada Oeste, Spain.

In order to analyze the response of the treatment to the different concentrations of CEC in the influent, experiments were conducted by varying the initial concentration in the samples. To prepare the samples in the laboratory, three dissolutions with different concentrations of ibuprofen, carbamazepine and ciprofloxacin were elaborated in three 1-L bottles, using as a matrix the water treated biologically. Later, the dissolutions were sonicated for 30 min to ensure the maximum solubility of the medicaments

in the water. The treated wastewater used in AOPs were then spiked with the appropriate volume of the corresponding solution according to the experiment and kept under stirring for 30 min before being treated in the photoreactor. A later measure of the spiked blends determined that those spiked with the first doping contained 59.83 μg/L of carbamazepine, 22.30 μg/L of ciprofloxacin and 54.60 μg/L of ibuprofen. Blends spiked with the second doping contained 95.03 μg/L of carbamazepine, 17.17 μg/L of ciprofloxacin and 69.60 μg/L of ibuprofen. At last, concentrations of 281.00, 98.53 and 275.00 μg/L of carbamazepine, ciprofloxacin and ibuprofen, respectively, were found in blends spiked with the third doping.

Each one of the three spiked water blends was tested under three different concentrations of hydrogen peroxide: 25, 50 and 100 mg/L. Each spiked water sample was introduced into the photoreactor, putting into operation at that moment the UV lamp and the cooling system. After a UV lamp run-up phase between 2 and 5 min, and once the temperature was steady at 20 ± 1 °C, the appropriate dosage of the oxidant agent was added, keeping the reaction medium in continuous agitation during the whole process. The properties of the collected water, whose pH and TOC was 6.67 and 22.69 mg/L respectively, remained intact before the AOP treatment.

To analyze the kinetics of removal of each contaminant in the different experiments, 50 mL samples were taken at 0, 10, 20 and 40 min. Sodic sulfite, which acts as a hydroxyl radical scavenger, was added in stoichiometric proportions to inhibit the oxidation of the pollutants in the taken samples. After stopping the reaction, the samples were frozen.

In order to assess the effect of the addition of catalysts on the efficiency of the process, the same experiments were carried out again but adding Fe^{2+} or TiO_2. The concentration of catalyst was established on 40 mg/L Fe^{2+} from ferrous sulfate at the photo-Fenton process and 1000 mg/L TiO_2 at the heterogeneous photocatalysis (Salimi et al. 2017). Since the evaluation of the feasibility of both photo-Fenton and heterogeneous process to removal CEC in urban wastewater effluents at natural pH is not widely studied, the pH (6.67) of the spiked wastewater blends was also not modified.

3.3. Physical and chemical determinations

To characterize the biologically treated urban wastewater used on the experiments, the pH and organic matter content were measured before the AOP treatment. The pH was determined by using a pH meter Crison pH 25®. Organic matter content was measured as TOC by using a Formacs HT TOC/TN Analyzer.

Pharmaceutical concentration in the samples was measured according to an analytic method based on the works previously reported by Garrido et al. (2016) and Martín et al. (2015). Once samples were filtered through 1.2-μm glass fiber membrane filters, the target compounds present in both dissolved and solid fractions were extracted by solid-phase extraction and sonication, respectively. On the one hand, the permeate was acidified to pH 2 and percolated through Oasis HLB SPE cartridges at a constant flow rate before the elution with methanol. On the other hand, the retentate was lyophilized in a Cryodos-50 lyophilizer and treated with methanol acidified

with 5 % of acetic acid. Then, it was sonicated for 10 min and centrifuged at 4000 rpm for other 20 min. Finally, the resultant supernatant was treated by dispersive solid-phase extraction using C18 sorbent and the organic phase containing the target compounds was separated by a centrifugation at 4000 rpm for 10 min. The aliquots containing the target compounds of both liquid and solid phases were evaporated with a nitrogen stream and the resultant residue was immediately analyzed by liquid chromatography-triple quadrupole mass spectrometry (LCQqQ-MS/MS) once dissolved in methanol/water (50:50, v/v) and percolated through a 0.22-μm nylon filter.

The analytical method was validated according to the extraction process recovery, precision, linearity and method detection and quantification limits (MDL and MQL, respectively) (Table 5). The extraction process recovery was measured by the difference of the peak areas of the target compound in the samples before and after the extraction (solutions A and B, respectively): R (%) = (A/B) × 100. The precision was estimated in terms of relative standard deviation (RSD) with measures in triplicate. The linearity was evaluated after the measure in triplicate of the standard solutions. MDL and MQL limits were determined as the concentrations corresponding to a signal-to-noise ratio of 3:1 and 10:1, respectively.

Table 5. Recovery, precision, linearity, method detection limit (MDL) and method quantification limit (MQL) for the target compounds in wastewater and sludge samples

Wastewater samples					
Compound	Recovery (%)	Precision (%)	Linearity (r^2)	MDL (μg/L)	MQL (μg/L)
Ibuprofen	89	10.0	0.994	0.012	0.039
Carbamazepine	120	2.9	0.999	0.001	0.002
Ciprofloxacin	91	4.8	0.997	0.150	0.730

Compound	Sludge samples				
	Recovery (%)	Precision (%)	Linearity (r^2)	MDL (µg/kg)	MQL (µg/kg)
Ibuprofen	59	19.0	0.998	1.41	4.54
Carbamazepine	69	10.0	0.999	0.10	0.25
Ciprofloxacin	89	6.1	0.999	13.20	69.10

3.4. Kinetic modeling

The main purposes of the kinetic modeling are, on the one hand, to understand the mechanism of the reaction and, on the other hand, to find out the degradation rate and its relationship with the operating parameters such as time, peroxide concentration, pH, light intensity and concentration of catalyst (Haroune et al. 2014; Carabin et al. 2015; Liao et al. 2016).

The degradation capacity of the tested CEC was evaluated by the calculation of the degradation rate from the adjustment to different kinetic models using the experimental data of concentration of the samples taken from the photoreactor at different time intervals. The models evaluated in this report are those commonly used to describe the mechanisms of reaction of elementary chemical reactions: zero-, first-, second-, third-, pseudo-first- and pseudo-second-order kinetic models.

3.5. Statistical analysis

The operative variables of the AOP (concentration of peroxide, initial concentration of CEC, the presence of catalyst) were included in a multivariate analysis using Canoco version 4.5 for Windows. This analysis

was used to quantify the influence of the variables on the behavior of the process (degradation rate, concentration in equilibrium and total degradation percentage as k, C_e and η, respectively), performing a Monte Carlo test (499 permutations) with a selected significance level of 0.05.

4. Results and discussion

4.1. Degradation efficiencies

Figure 4 shows the degradation percentages of each micropollutant in all the experiments. The rows show experiments carried out at the same initial concentration of CEC, and the columns show experiments carried out at the same peroxide dosage.

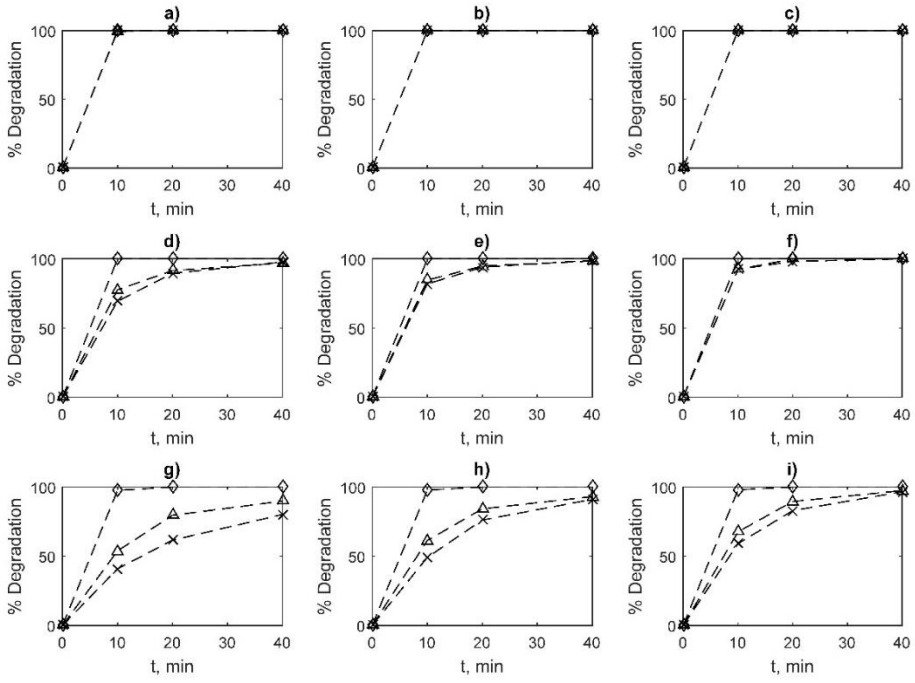

Figure 4. Degradation efficiencies of carbamazepine (-⤬-), ciprofloxacin (-⧫-) and ibuprofen (-▲-) during the treatment of dopings 1 (a, b, c), 2 (d, e, f) and 3 (g, h, i) under 25 (a, d, g), 50 (b, e, h) and 100 mg/L of oxidant (c, f, i)

During the first 10 min of treatment, major degradation of the pollutants was observed in all the experiments, independently of the initial concentration of CEC and the peroxide dosage.

Among the three CEC analyzed in the domestic wastewater, ciprofloxacin presented the highest degradation efficiency. This pharmaceutical presented a complete degradation in all the experiments after 20 min of treatment.

Moreover, it can be noted that carbamazepine and ibuprofen showed similar degradation efficiencies, but lower than those obtained for ciprofloxacin. At the lowest concentration experiments (59.83 and 54.60 μg/L for carbamazepine and ibuprofen, respectively), they were completely degraded in 10 min using a peroxide dosage from 50 mg/L (see experiments a, b and c in Figure 4). The degradation efficiency of both compounds exceeded 97 % after 40 min of treatment for any peroxide dosage tested in the experiments carried out at moderately higher concentrations, 95.03 μg/L of carbamazepine and 69.60 μg/L of ibuprofen (experiments d, e and f in Figure 4). When CEC concentrations much higher than those usual in urban wastewater were evaluated, the different degradability of both compounds became more appreciable, with ibuprofen presenting a minimum degradation of 89.83 % and a maximum of 97.39 % and carbamazepine between 80.14 and 96.56 % at the different conditions tested (experiments g, h and i in Figure 4).

Similar removal efficiencies were found in the literature in cases of CEC removal from urban wastewater by photoassisted H_2O_2/UV AOP at near neutral pH. De la Cruz et al. (2012) found in the secondary settler effluent of a WWTP in Switzerland, 29.5 μg/L of a mix of 32 CEC that had not been removed by the biological treatment, among which were found ciprofloxacin, carbamazepine and ibuprofen (De la Cruz et al. 2012). Without altering the properties of the biologically treated urban wastewater (pH of 7.42 and 15.93 mg/L TOC), they obtained removal efficiencies of 69 % for ciprofloxacin, 75 % for carbamazepine and 100 % for ibuprofen in 10 min of treatment using AOP with 50 mg/L of H_2O_2. A complete removal efficiency of all of them was obtained after 30 min of operation. Afonso-Olivares et al. (2016) also used a H_2O_2/UV AOP to remove 23 pharmaceuticals from a secondary effluent of an urban WWTP, whose pH and carbon content were 7.97 and 20.42 mg/L, respectively (Afonso-Olivares et al. 2016). With different peroxide dosages ranging from 5 to 25 mg/L, they achieved an almost complete degradation of ciprofloxacin in 5 min. However, carbamazepine was more slowly degraded by the UV/H_2O_2 treatment; removal near to 60 % for carbamazepine in 40 min of treatment was achieved. They obtained a degradation of ibuprofen that ranged from 67 to 99 % according to the added peroxide dosage.

4.2. Degradation rate assessment

In Table 6, for each pharmaceutical, the values of the experimental degradation rates are shown, calculated from the adjustment to the different kinetic models. The correlation coefficient of each adjustment is also shown.

As can be observed in Table 6, the average correlation coefficients of zero-, second-, third- and pseudo-secondorder kinetic models were all less than 0.9000 for each pharmaceutical. It indicates that these 4 kinetic models are not suitable for interpreting the mechanism of degradation of these micropollutants in wastewater by using the photoassisted H_2O_2/UV AOP.

The first-order kinetic model presented an average correlation coefficient considerably higher than those obtained in the previous kinetic models (R^2 = 0.9787 for carbamazepine, R^2 = 0.9875 for ciprofloxacin and R^2 = 0.9319 for ibuprofen). However, these values are not considered high enough to affirm that the degradation of these micropollutants is governed by a first-order kinetic.

Instead, as can be seen in Table 6, the pseudo-first-order model was the kinetic model that best fits the empirical data obtained, presenting an average value of 0.9935 in its correlation coefficient for carbamazepine, of 0.9999 for ciprofloxacin and of 0.9900 for ibuprofen. Thus, the degradation of the pollutants tested clearly follows a pseudo-first-order kinetic.

Table 6. Degradation rate values and average correlation coefficients of the different kinetic models

CEC	Operative conditions		Order Zero	First Order	Second Order	Third Order	Pseudo-first Order	Pseudo-second Order
	Doping	$[H_2O_2]$, mg/L	k, min^{-1}	k, min^{-1}	L/(mg·min)	$L^2/(mg^2 \cdot min)$	k, min^{-1}	L/(mg·min)
CBZ	1	25	5.9832	1.0999	99.9983	50000.0000	1.0999	99.9983
	2	50	5.9832	1.0999	99.9983	50000.0000	1.0999	99.9983
	3	100	5.9832	1.0999	99.9983	50000.0000	1.0999	99.9983
	1	25	2.8936	0.0994	0.0097	0.0021	0.1198	0.0097
	2	50	3.0132	0.1224	0.0214	0.0105	0.1538	0.0214
	3	100	3.1167	0.2684	19.0532	9523.8110	0.2684	19.0532
	1	25	6.4848	0.0424	0.0003	~ 0	0.0610	0.0003
	2	50	7.5686	0.0629	0.0008	~ 0	0.0788	0.0008
	3	100	8.1770	0.0853	0.0021	0.0001	0.0902	0.0021
	Averag correlation coef		0.5417	0.9787	0.8465	0.7492	0.9935	0.8465
CPX	1	25	2.2150	0.5002	0.6622	2.2221	0.5002	0.6622
	2	50	2.2150	0.5002	0.6622	2.2221	0.5002	0.6622
	3	100	2.2150	0.5002	0.6622	2.2221	0.5002	0.6622
	1	25	1.7017	0.4740	0.6608	2.2221	0.4740	0.6608
	2	50	1.7017	0.4740	0.6608	2.2221	0.4740	0.6608
	3	100	1.7017	0.4740	0.6608	2.2221	0.4740	0.6608
	1	25	5.8582	0.3339	0.2744	0.8906	0.3759	0.2744
	2	50	5.8628	0.3359	0.2753	0.8910	0.3870	0.2753
	3	100	5.8664	0.3377	0.2762	0.8914	0.3966	0.2762
	Averag correlation coef		0.7185	0.9875	0.7608	0.7043	0.9999	0.7608
IBP	1	25	3.2709	0.4463	3.4192	139.0779	0.5519	3.4192
	2	50	5.4588	0.8423	8.3315	347.2222	0.8423	8.3315
	3	100	5.4588	0.8423	8.3315	347.2222	0.8423	8.3315
	1	25	2.1493	0.0972	0.0105	0.0023	0.1458	0.0105
	2	50	2.2140	0.1164	0.0202	0.0085	0.1711	0.0202
	3	100	4.0689	0.3980	3.3362	138.8892	0.3980	3.3362
	1	25	7.4937	0.0623	0.0008	~ 0	0.0989	0.0008
	2	50	7.8841	0.0729	0.0011	~ 0	0.1108	0.0011
	3	100	8.3315	0.0963	0.0029	0.0002	0.1204	0.0029
	Averag correlation coef		0.5567	0.9319	0.8720	0.7677	0.9900	0.8720

Apparently, this fact contrasts with the premise seen previously (Eq. 3), in which CEC are directly oxidized by the hydroxyl radicals. Nevertheless, the concentration of peroxide is usually much higher than that of the micropollutants in these kinds of experiments, and consequently, the concentration of hydroxyl radicals $[OH^{\cdot}]$ in the reaction medium is also much higher than the concentration of CEC, $[OH^{\cdot}] \gg [CEC]$ (Giannakis et al. 2015; Shu et al. 2016). Therefore, while the concentration of CEC changed from C_0 to C_e , the concentration of $OH^{\cdot}$ remained essentially constant at a value equal to $[OH^{\cdot}]_0$, so the degradation rate equation could be written as follows (Eq. 4), where $k_{ap} = k \cdot [OH^{\cdot}]$.

$$v = -\frac{d[CEC]}{dt} = k_{ap} \cdot [CEC] \quad (4)$$

This fact would explain that the degradation of the micropollutants by using photo-assisted H_2O_2/UV AOP follows a pseudo-first-order kinetic, which agrees with Shu et al. (2013). Other authors also showed in similar experiments that the degradation of these kind of pollutants using H_2O_2/UV AOP follows a pseudo-first-order kinetic (Pereira et al. 2007; Kim et al. 2009).

The experimental degradation rates obtained for carbamazepine (from 0.0703 to 1.0999 min^{-1}, shown in Table 6) agree with values reported in the literature for similar cases (Pereira et al. 2007; Kim et al. 2009; Giannakis et al. 2015). In the study conducted by Pereira et al. (2007), a blend of water with pH 7 and 4.2 mg/L of dissolved organic carbon from a lake was treated by photo-assisted H_2O_2/UV AOP with a dosage of 10 mg/L of H_2O_2, obtaining a pseudofirst kinetic degradation rate of 0.22 min^{-1}. Giannakis et

al. delivered as a result a pseudo-first-order kinetic degradation rate of 0.644 min^{-1} for the degradation of carbamazepine from an effluent of a MBBR process with pH 7.4 and 20.2 mg/L TOC, using a dosage of 25 mg/L of H_2O_2 in an H_2O_2/UV AOP. Kim et al. (2009) also experimented with the degradation of carbamazepine in a secondary effluent from a sewage treatment plant spiked with CEC. They achieved a degradation rate of 0.09 min^{-1} by adjusting the concentration data to a pseudo-first-order kinetic model in a treatment with a dose of 8.2 mg/L of peroxide.

With respect to the degradation rates for ibuprofen calculated in the present study (from 0.0989 to 0.8423 min^{-1} as Table 6 shows), very similar pseudo-first-order kinetic rates were also found in the study of Shu et al. (2013). The degradation rates for ibuprofen in spiked water without organic matter and with pH 7 ranged from 0.38 to 0.56 min^{-1} depending on the H_2O_2 dosage (25 – 50 mg/L) in an H_2O_2/UV AOP.

No values of pseudo-first-order degradation rate for ciprofloxacin by using photo-assisted H_2O_2/UV AOP were found in the literature, so the values obtained in this report (0.3759 – 0.5002 min^{-1}, shown in Table 6) could not be contrasted.

4.3. Influence of the operative variables

Figure 5 shows the influence of the operative variables on the results of the photo-assisted H_2O_2/UV AOP evaluated in this article. The correlation between the variables (red lines) and the species (black lines) is shown from the length of the vectors and the relative angles between them. The greater the length of the vector, the greater its influence on the variability of the system. In relation to the angle, the smaller it is, the greater the correlation: Thus, angles close to 30° indicate a strong positive correlation and angles greater than 120° imply a strong negative correlation. Angles close to 90° show the absence of relationship between the vectors.

Effect of initial CEC concentration

With the variation of the initial concentration, ibuprofen and carbamazepine showed statistically significant differences in the total removal efficiencies of the process. It was not the case for ciprofloxacin, since it showed a removal yield of 100% in all the experiments, regardless of the initial concentration tested (Figure 4).

As it can be analyzed in the Canoco diagram for carbamazepine and ibuprofen (Figure 5), the higher the initial concentration of the pollutants in the process is, the lower the degradation yields of the pollutants are. From experimental results, it can furthermore be extracted that this effect is mainly accentuated in the first minutes of treatment, and the effect is diluted with time due to the asymptotic trend of the degradation kinetic observed.

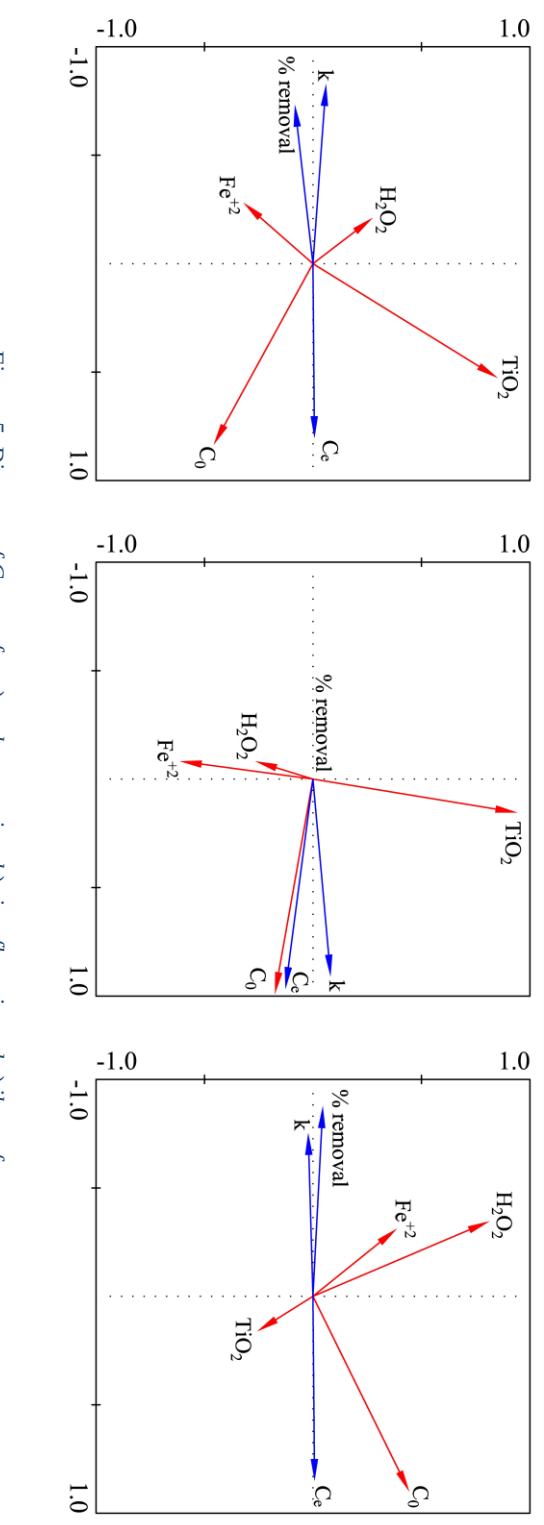

Figure 5. Diagram of Canoco for a) carbamazepine, b) ciprofloxacin and c) ibuprofen

The decrease in degradation efficiencies that occurs when the initial concentration of pharmaceuticals in water is increased can be explained by comparing the calculated degradation rates for each compound at the different initial concentrations tested. As can be observed in Table 6, a statistically significant decrease in the degradation rate occurs with higher initial concentrations of pollutants. These results reveal that the degradation rate of each pollutant depends on its initial concentration.

A few reports investigate the degradation kinetics of CEC by H_2O_2/UV AOP at various initial concentration levels. The report realized by Shu et al. (2013) is one of them. They also observed that the degradation constant of several studied CEC is a function of its initial concentration, which may be due to higher initial concentrations of micropollutants producing larger amounts of by-products that could interact with hydroxyl radicals, so the degradation rate decreases.

According to this hypothesis, the decomposition of higher concentrations of micropollutants would originate a greater quantity of by-products susceptible to react with hydroxyl radicals, which could justify the drastic decrease observed in the value of the degradation rates for ibuprofen and carbamazepine when the concentration of both pollutants increased considerably in water (up to 275 μg/L and 281 μg/L, respectively). On the other hand, the less pronounced decrease in the degradation rate values for ciprofloxacin could be due to its lower concentration in water.

Effect of oxidant dosage

As it can be analyzed in the Canoco diagrams (Figure 5) and checked in Figure 4, the degradation efficiency of the CEC increases slightly with the increase in the peroxide dosage. In the same way, the degradation rates reported in Table 6 reveal that higher concentrations of H_2O_2 improve the degradation of the pollutants tested.

This improvement can be attributed to the generation of a higher hydroxyl radical concentration by the photochemical decomposition of the H_2O_2 added (Alharbi et al. 2017). The value of the degradation rate increases linearly with the increase in the hydroxyl radical concentration in water (Nihemaiti et al. 2018), according to the hypothesis made previously (Eq. 4).

However, the increase in the degradation rate was not statistically significant and it is observed in the experimental data that an increase in the peroxide dosage from 25 mg/L to 50 or 100 mg/L did not result in a linear increase in the degradation rate value according to the equation. In particular, the degradation rate for carbamazepine was enhanced by 1.28 – 1.29 times and 1.47 – 2.24 times by increasing the peroxide dosage from 25 mg/L to 50 and 100 mg/L, respectively. In the same way, the increase in the values of the degradation rates for ibuprofen also did not present a linear behavior, where between 1.12 – 1.53 and 1.21 – 2.73 higher values were obtained for 50 and 100 mg/L, respectively, in comparison with a dosage of 25 mg/L. A special case is ciprofloxacin, due to the fact that its prompt

degradation resulted in an insignificantly improvement on the degradation rate with the addition of a higher concentration of peroxide.

This could be due to the appearance of quenching reactions. It has been reported that from an optimal concentration of peroxide, the addition of higher concentrations may limit the degradation rate due to the quenching of the hydroxyl radicals based on the reactions described by Poyatos et al. (2010) and Liao et al. (2016). The generation of a higher concentration of hydroxyl species in water may promote the reaction with residual peroxide, with $HO_2^{\cdot}$, or even between themselves, so that the increase in degradation rate ceases to be lineal with the peroxide concentration (Fast et al. 2017).

Effect of catalyst addition

To assess the possible improvements with the use of catalysts in the photo-assisted H_2O_2/UV AOP, the same experiments were carried out at the same experimental conditions. Figure 6, Figure 7 and Figure 8 show for carbamazepine, ciprofloxacin and ibuprofen, respectively, the degradation yields obtained in the two photocatalyzed processes compared to those obtained with the process without a catalyst. Table 7 shows the comparison between the degradation rates obtained in each experiment at the three different processes.

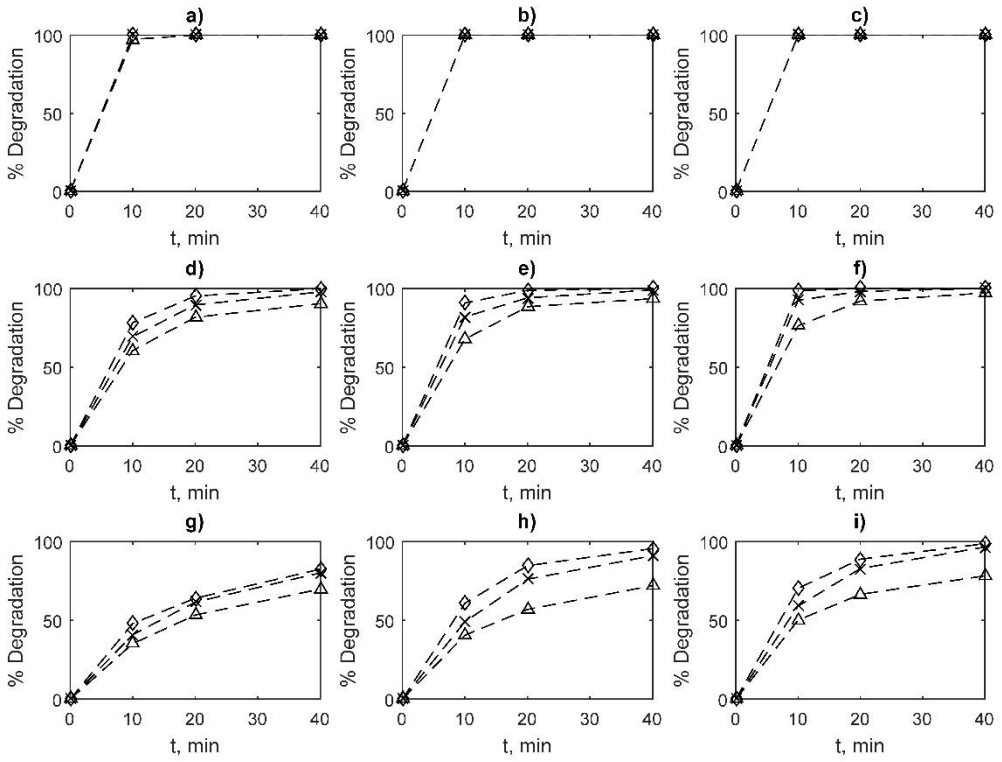

Figure 6. Degradation of carbamazepine by H_2O_2/UV (x), Fe^{2+}/H_2O_2/UV (◊) and TiO_2/H_2O_2/UV (Δ) during the treatment of dopings 1 (a-c), 2 (d-f) and 3 (g-i) using 25 (a, d, g), 50 (b, e, h) and 100 mg/L of H_2O_2 (c, f, i)

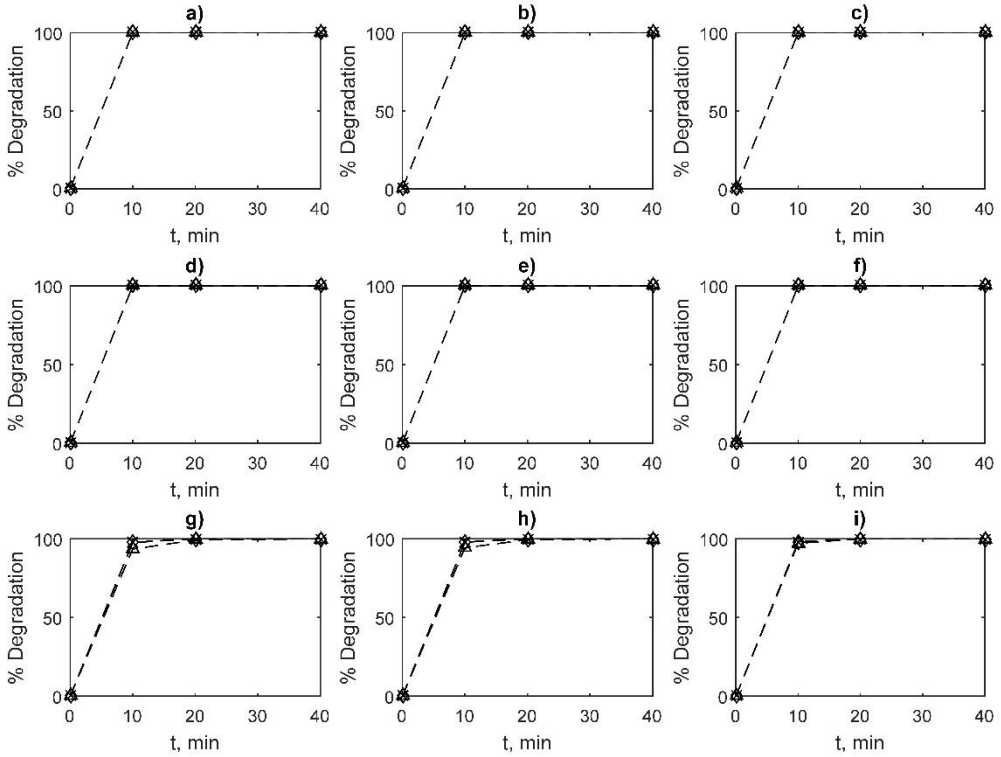

Figure 7. Degradation of ciprofloxacin by H_2O_2/UV (x), Fe^{2+}/H_2O_2/UV (◊) and TiO_2/H_2O_2/UV (Δ) during the treatment of dopings 1 (a-c), 2 (d-f) and 3 (g-i) using 25 (a, d, g), 50 (b, e, h) and 100 mg/L of H_2O_2 (c, f, i)

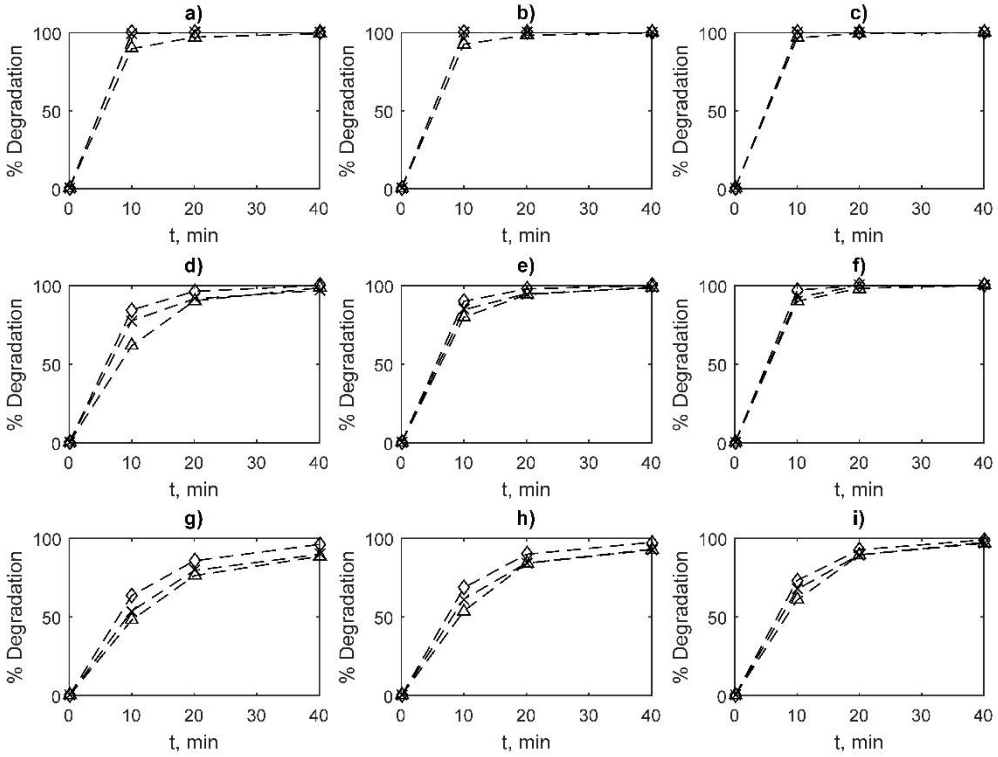

Figure 8. Degradation of ibuprofen by H_2O_2/UV (x), Fe^{2+}/H_2O_2/UV (◊) and TiO_2/H_2O_2/UV (Δ) during the treatment of dopings 1 (a-c), 2 (d-f) and 3 (g-i) using 25 (a, d, g), 50 (b, e, h) and 100 mg/L of H_2O_2 (c, f, i)

Photo-Fenton AOP The results obtained in the photo-Fenton experiments, for a dosage of 40 mg/L of Fe^{2+}, are shown in Table 7. In this table, it can be observed clearly that pharmaceuticals degradation rates are in all experiments equal or higher, to a greater or lesser degree, than those of the without-catalyst process. This improvement degree with respect to the without-catalyst process depended to a large extent of the initial concentration of CEC and to a much lesser extent on the peroxide dosage.

As the initial concentration of CEC was lower, it can be appreciated how the difference between degradation rate values with and without catalyst becomes more noticeable until reaching a point where the concentrations are such that they are completely removed before the first sample is taken (10 min) in both the catalyzed and uncatalyzed processes, so the degradation rate value of the catalyzed process becomes the same of that of the uncatalyzed process.

However, the improvement obtained in the degradation rate with respect to the uncatalyzed process was negligible at high initial concentrations of micropollutants and insufficient at low concentrations to have a statistically significant impact on their removal yields (see Figure 6, Figure 7 and Figure 8), as it happens in the acidic pH photo-Fenton process (Klamerth et al. 2013).

Table 7. Pseudo-first order degradation rates for carbamazepine, ciprofloxacin and ibuprofen at the different catalyzed processes evaluated: H_2O_2/UV AOP, Fe^{2+}/H_2O_2/UV AOP and TiO_2/H_2O_2/UV AOP.

		Carbamazepine			Ciprofloxacin			Ibuprofen		
Operative conditions		H_2O_2/UV AOP	Fe^{2+}/H_2O_2/UV AOP	TiO_2/H_2O_2/UV AOP	H_2O_2/UV AOP	Fe^{2+}/H_2O_2/UV AOP	TiO_2/H_2O_2/UV AOP	H_2O_2/UV AOP	Fe^{2+}/H_2O_2/UV AOP	TiO_2/H_2O_2/UV AOP
Dop	[H_2O_2], mg/L									
1	25	1.0999	1.0999	0.5123	0.5002	0.5002	0.5002	0.5519	0.8423	0.1996
	50	1.0999	1.0999	1.0999	0.5002	0.5002	0.5002	0.8423	0.8423	0.2192
	100	1.0999	1.0999	1.0999	0.5002	0.5002	0.5002	0.8423	0.8423	0.3058
2	25	0.1198	0.1590	0.1114	0.4740	0.4740	0.4740	0.1458	0.2053	0.1147
	50	0.1538	0.2713	0.1395	0.4740	0.4740	0.4740	0.1711	0.2126	0.1522
	100	0.2684	0.5445	0.1460	0.4740	0.4740	0.4740	0.3980	0.4173	0.2147
3	25	0.0610	0.0686	0.0597	0.3759	0.3865	0.2559	0.0989	0.1056	0.0870
	50	0.0788	0.1017	0.0696	0.3870	0.3944	0.2716	0.1108	0.1228	0.1079
	100	0.0902	0.1133	0.0902	0.3966	0.4017	0.3560	0.1204	0.1349	0.1187

Specially, in the case of carbamazepine, the difference between the degradation rate values between the catalyzed and uncatalyzed processes varied from 0.0076 min^{-1} at the highest concentrations to 0.2761 min^{-1} at the lowest concentrations. This one resulted in an improvement in the removal yields only up to 4.45 % after 40 min of treatment.

The increase in ciprofloxacin degradation rate was practically negligible, being at best 0.0106 min^{-1}. The improvement in the degradation yield was, in all cases, less than 1 %.

The effect of iron added in the blends contributed to the improvement in the ibuprofen degradation rate in a similar way to the carbamazepine degradation rate. The degradation rate increased its value from 0.0066 to 0.2904 min^{-1}, which was not even enough to increase the degradation percentage beyond 6.28 % after 40 min of treatment.

The poor enhancement observed may probably be due to the fact that ferric ions hardly make organic substances available with which to form complexes, inhibiting the catalytic process since iron does not form complexes with aqueous species at near neutral pH levels. A similar evaluation was carried out by De la Cruz et al. (2012). They studied the degradation of several CEC, with carbamazepine, ciprofloxacin and ibuprofen included, with a H_2O_2/UV AOP, and they also compared the results when 25 and 50 mg/L of Fe^{2+} were added to the process (De la Cruz et al. 2012). The pH of the wastewater was 7.42, and the TOC concentration

was 15.93 mg/L. Their results showed that there was no improvement in the degradation of these CEC when iron was added.

Heterogeneous photocatalysis Results obtained by this process using 1000 mg/L of TiO_2 are compared with those obtained in H_2O_2/UV and photo-Fenton processes in Table 7. Far from increasing the degradation rates of the three pharmaceuticals, the addition of TiO_2 as a catalyst produced lower degradation rates than those of the uncatalyzed process. The consequence was an impoverishment of the degradation yields, especially for carbamazepine (Figure 6, Figure 7 and Figure 8).

In particular, removal percentages for carbamazepine were below 80 and even 70 %, resulting in removal losses close to 20 % in the experiments with the highest concentrations, compared to the uncatalyzed process. However, a lower decrease was shown by ibuprofen and ciprofloxacin. Ibuprofen showed a much lesser pronounced decrease in its removal performance, in line with the impoverishment of the degradation rate, while the low concentration of ciprofloxacin did not affect its performance.

The cause of the decrease in degradation rates could be due to an excess of the catalyst dosage. Several cases of efficiency losses caused by this reason have been reported. It is noted that light penetration and the number of active sites provided by the addition of the catalyst are two of the most important conditions that limit heterogeneous photocatalysis (Villegas-Guzman et al. 2015). As the catalyst concentration added to the process increases, degradation rate of organic pollutants increases due to the

increment of the number of available active sites. However, there is an optimal concentration, depending on the characteristics of catalyst and pollutants and on the light pathways in the reactor design, from which a light screening begins to take place (Jallouli et al. 2018). This event is likely to inhibit the degradation rate improvement or even decrease its value.

An evident increase in the turbidity of the water blends was observed during the loading of the catalyst to the photoreactor. The presence of such a high catalyst particles concentration gave the reaction medium a relatively opaque white color. Such a degree of opacity could have caused screening that prevented the penetration of the UV light destined to reach the peroxide molecules (Carabin et al. 2015), inhibiting the generation of hydroxyl radicals, and therefore, the degradation of CEC.

It is important to point out that the lower values of degradation observed for carbamazepine with respect to the other two pharmaceuticals could have been due to different direct interactions between titanium dioxide and the pharmaceuticals. At the natural pH of the biological treated blends (6.67), the molecules of ciprofloxacin and ibuprofen would be negatively charged according to their pKa values, 6.15 and 4.9, respectively (Eskandari et al. 2017; Jallouli et al. 2018), while carbamazepine, having a pKa higher (13.9) than the pH of the water, would remain in molecular form, not being ionized (Mohapatra et al. 2014). Since the pH of the aqueous medium is slightly lower than the isoelectric point of the TiO_2, it is taken for granted, and in view of the results, that catalyst particles presented a certain positive charge on their surface. Consequently, electrostatic interactions

between the positive charge of titanium dioxide and the negatively charged molecules of ciprofloxacin and ibuprofen favored the degradation of these micropollutants, while the worst affinity between undissociated carbamazepine and positively charged titanium dioxide particles would justify the significantly lower degradation percentages.

5. Conclusions

From the results obtained with a photo-assisted AOP operating as a tertiary treatment to remove different concentrations of a mix of CEC (carbamazepine, ciprofloxacin and ibuprofen) in a real urban wastewater effluent using 25, 50 and 100 mg/L of hydrogen peroxide at the natural pH and 20 ºC, the following conclusions were attained:

- The degradation efficiencies obtained for carbamazepine and ibuprofen after 40 min of treatment ranged between 80.1 – 100 and 89.8 – 100 %, respectively, while ciprofloxacin was totally degraded even before 20 min.
- The best adjustment for the degradation of tested CEC was obtained with a pseudo-first-order kinetic model ($R^2 > 0.99$).
- The degradation rates of the tested CEC were found to be strongly dependent on their initial concentration, and to a lesser extent, on the peroxide dosage. Experimental degradation rates from 0.0703 to 1.0999 min^{-1} were obtained for carbamazepine, from 0.3759 to 0.5002 min^{-1} for ciprofloxacin, and from 0.0989 to 0.8423 min^{-1} for ibuprofen.

- In the presence of 40 mg/L of Fe^{2+} (Photo-Fenton, $Fe^{+2}/H_2O_2/UV$), a statistically significant improvement on the degradation of CEC was not observed, while the addition of 1000 mg/L of TiO_2 (heterogeneous photocatalysis, $TiO_2/H_2O_2/UV$) resulted in a light screening that at the same time resulted in degradation efficiencies lower than those obtained in the process without a catalyst.

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V - CHAPTER 2

Removal of a pharmaceutical mix from urban wastewater coupling membrane bioreactor with advanced oxidation processes.

V - CHAPTER 2

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1. Abstract

Emerging contaminants are a global concern, as Directive 2013/39/UE shows. Given the possible consequences that may lead to the presence of these compounds in water resources, different proposals are being evaluated to avoid their discharge into the environment. This study focuses on the use of a biological and physicochemical combined treatment formed by a membrane bioreactor with an H_2O_2/UltraViolet (UV) advanced oxidation process coupled subsequently to degrade contaminants of emerging concern in real urban wastewater. The membrane bioreactor operated at 16 h of hydraulic retention time and 4250 mg/L of mixed liquor

suspended solids. Different hydrogen peroxide dosages (25, 50, and 100 mg/L) were tested in the photoreactor at 20 ºC and the natural pH of the wastewater. Different initial concentrations of a mix of pharmaceuticals (carbamazepine, ciprofloxacin, and ibuprofen) were tested. Removal efficiencies obtained in the biological stage ranged from 66.23 – 96.18 %, 90.63 – 100%, and 90.04 – 96.48 %, respectively. However, complete removal was achieved after the physicochemical stage when the concentrations of contaminants in the mix were similar to current concentration levels in urban wastewater.

2. Introduction

From their origin, urban wastewater treatment plants (WWTPs) have taken advantage of biological processes, based on the metabolic activity of certain microorganisms contained in urban wastewater, to carry out the removal of the undesirable substances that are found in them, traditionally suspended solids and organic matter. However, the growing concentration of urban areas and progressive increase of industrial activity have led concurrently to an increase in the presence of new pollutants in the wastewater from human activities (Pal et al. 2014). Among them, there is a group of contaminants commonly called contaminants of emerging concern (CECs), formed by a wide range of unregulated chemical compounds, which include substances such as pharmaceuticals, pesticides, illicit drugs, or personal care products (Hamza et al. 2016).

Most of these pollutants are characterized as being substances hardly degradable biologically or even totally persistent, so conventional activated sludge (CAS) technology has little effect toward the degradation of most of these compounds (Aamand et al. 2015). Because they do not undergo a complete removal, CECs are discharged into the receiving environment. Also, although the concentration levels are currently low (from ng/L to μg/L), they are beginning to be considered potentially dangerous. The discharge of antibiotics can induce the acquisition of antibiotic resistance genes, giving rise to the development of antibiotic-resistant organisms in water resources susceptible to purification and subsequent consumption. This fact has triggered a global social alarm that threatens to endanger the public health of society (Kumar and Pal 2018).

Despite the fact that CECs are not currently covered under existing water quality regulations in the European Union (EU), the entry in vigor of the Directive 2013/39/EU has allowed many of them to be included in a watch list (Decision 2015/495/EU) according to Directive 2000/60/CE. Consequently, the substances included in this list could be reclassified as priority substances subject to regulation. This provides a strong drive in the development of research lines whose objects are to identify and evaluate alternative advanced treatments able to adapt to CAS technology and complement the removal of these pollutants in urban WWTPs.

The reconversion of a CAS bioreactor into a membrane bioreactor (MBR) is a biotechnological proposal successfully employed in the treatment of urban wastewaters. Apart from providing high water quality with respect

to CAS processes, these systems significantly improve the removal of CEC. The higher yields of the MBR compared to the CAS process are because, among other aspects, they provide higher solid retention times, which favors (1) the removal by sorption onto the sludge and subsequent biodegradation and (2) the growth of more specific microorganisms in the degradation of certain contaminants (Wijekoon et al. 2013). In the last years, the removal of CECs by using MBR has been assessed, getting great results. However, this technology can not remove the entirety of these pollutants because many of them are practically persistent (Taylor et al. 2015).

The use of physicochemical treatments, such as the advanced oxidation process (AOP), is convenient to remove the nonbiodegradable fraction. The AOP is based on physicochemical reactions involving the in situ generation of hydroxyl radicals whose oxidation potential is such that they can degrade the chemical structure of the most persistent compounds (Oturan and Aaron 2014). Although AOP systems are the most used for the removal of CEC because they can remove practically any contaminant, their use in urban WWTPs is prohibitive because of the high energy consumption and because their efficiency is reduced by the presence of particles.

Few studies have evaluated the use of integrated approaches that combine physicochemical and biological treatment processes, such as a combined MBR-AOP process, to treat wastewater containing CECs. The reconversion of a CAS bioreactor into a MBR could remove particles by means of the membranes and previously remove a higher load of CEC at the entry of the photoreactor, which could increase the removal efficiency of the

AOP and also reduce the necessary treatment time, reducing the costs. Therefore, the use of the combination of both technologies could make viable the use of AOP as tertiary treatment in urban WWTPs.

The present research aims to study the removal capacity of three common CECs in urban wastewater (ciprofloxacin, carbamazepine, and ibuprofen) in an integrated system formed by a MBR with a subsequent AOP throughout the modeling process.

3. Materials and methods

3.1. Experimental set-up

The experimental setup used to carry out the research consisted of a pilot-scale MBR plant with a photoreactor coupled for the treatment of effluent with an AOP. In this way, physicochemical degradation was carried out in the photoreactor to the fraction of pharmaceuticals not biologically degraded in the MBR system (Figure 9). The pilot plant used for the research was fed with real urban wastewater from the WWTP "Los Vados" in Granada (Spain), where it was located. The MBR system was formed by a 272-L aerated bioreactor. The mixed liquor suspended solids (MLSS) in the bioreactor was driven by gravity to a 78-L rectangular tank where separation of the treated water was carried out by means of 4 hollow-fiber membrane modules of ultrafiltration ZW-10 (ZENON, Quebec). To avoid concentration of the MLSS on the outer surface of the membranes, a recirculation pump with a constant flow rate of 90 L/h (165 % of the influent) was used.

Furthermore, 24.34 L of excess sludge were daily extracted over the course of the project to keep the MLSS constant in the bioreactor.

Because several authors have shown that medium-pressure UltaViolet (UV) lamps are more efficient than low-pressure UV lamps when removing CEC by UV/H_2O_2 AOP (Pereira et al. 2007; Wols et al. 2013), the physicochemical treatment was performed in a photoreactor that included a medium-pressure mercury vapor lamp (150 W) with a wide emission spectrum in the UV range above 190 nm (UV-Consulting Peschl). The UV lamp was placed inside an immersion tube located in the center of a cylindrical batch reactor with 700 mL capacity. The immersion tube was provided with a water cooling jacket in order to dissipate the heat emitted by the lamp. Both immersion tube and cooling jacket were made of a quartz glass that allowed a transmission level above 92%. The reaction medium was maintained in constant agitation by means of a magnetic stirrer located below the reactor.

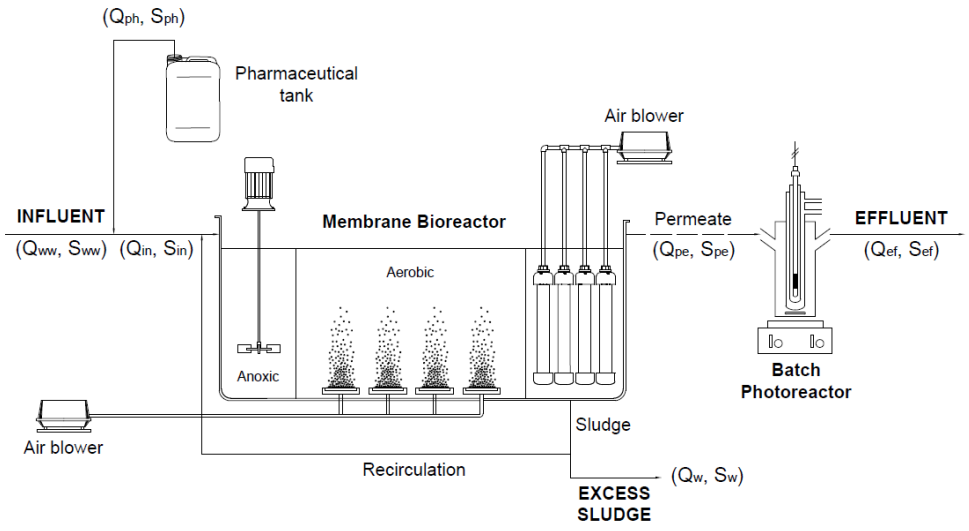

Figure 9. Experimental setup

3.2. Operation conditions and experimental procedure

In order to evaluate the synergetic effects on the removal of CECs when implementing the combined treatment in existing urban WWTPs, hydraulic retention time (HRT) and MLSS were fixed at 16 h and 4250.79 ± 495.82 mgMLSS/L, according to typical values in urban WWTPs working with MBR technology (Sun et al. 2016), whereas solid retention time (SRT) was imposed by the system working in such conditions (13.56 d). The experimental MBR pilot plant continuously treated real urban wastewater during the 42 days the experiment was ongoing. The first 15 days were necessary to accumulate the MLSS concentration established in the bioreactor. From this point, constant operative conditions of HRT and SRT were maintained during all the research. The pilot plant worked in a steady state during which the analysis corresponding to cycle 0 was carried out. Later, under the same operative conditions, the influent to the pilot plant was doped continuously with a mix of three common pharmaceuticals, which were chosen according to their presence in urban WWTPs and their physicochemical characteristics. These were a common and easily degradable nonsteroidal antiinflammatory drug such as ibuprofen, a biologically persistent and nondegradable by direct photolysis antiepileptic drug such as carbamazepine, and a strong sorption trend to biomass antibiotic drug such as ciprofloxacin (Kim et al. 2009; Sipma et al. 2010; Giri et al. 2011; Shu et al. 2013; Cecconet et al. 2017). These pharmaceuticals were added to the influent of the pilot plant under three different concentrations. The value of the lowest concentrations tested (Doping 1) was assigned as a

value slightly higher than the maximum concentrations found in the literature in order to ensure that the treatment of any concentration found today in urban wastewater was covered (Verlicchi et al. 2012; Tran et al. 2018; Gallardo-Altamirano et al. 2018). Concentrations of Dopings 2 and 3 were set 10 and 50 times higher to draw conclusions when the system is forced (Table 8). After a dilution time needed to ensure the corresponding concentration of CECs in the bioreactor (2 – 3 days, according to a mass balance), each doping was maintained until the absence of variations in the MBR: the sudden addition of pharmaceuticals resulted in a slight decrease of biomass (from 3610.61 ± 433.32 mg/L MLSS to 3345.05 ± 385.60 mg/L MLSS), which stabilized in 5 – 6 days. Once the operating conditions in the MBR were stable, the physicochemical treatment plant was put into operation and samples were taken from the bioreactor. During each doping, the effluent of the MBR plant was treated by AOP without any previous change in its pH. The UV radiation source was turned on at the same time that the cooling jacket was put into operation. The process was initiated with the addition of H_2O_2 after a run-up phase of between 2 and 5 min, during which emission of the light and temperature in the system were stabilized. The temperature was kept constant at 20.0 ± 0.5 °C in all the experiments, and dosages of 25, 50, and 100 mg/L of H_2O_2 were evaluated. Samples of 100 mL were withdrawn from the photoreactor after 0, 10, 20, and 40 min.

Table 8. Concentrations of carbamazepine, ciprofloxacin and ibuprofen in the influent and effluent of the MBR and average removal efficiencies

Carbamazepine			
Doping	Influent (µg/L)	Effluent (µg/L)	Removal (%)
1	100	33.77 ± 29.71	66.23 ± 29.71
2	1000	116.44 ± 7.50	88.36 ± 0.75
3	5000	190.78 ± 9.58	96.18 ± 0.19

Ciprofloxacin			
Doping	Influent (µg/L)	Effluent (µg/L)	Removal (%)
1	10	0.00 ± 0.00	≈ 100
2	100	6.88 ± 0.96	93.12 ± 0.96
3	500	46.84 ± 3.86	90.63 ± 0.77

Ibuprofen			
Doping	Influent (µg/L)	Effluent (µg/L)	Removal (%)
1	100	9.96 ± 11.41	90.04 ± 11.41
2	1000	77.16 ± 21.12	92.28 ± 2.11
3	5000	176.22 ± 16.26	96.48 ± 0.33

3.3. Physical and chemical determinations

Physical and chemical determinations were carried out for samples taken from influent, effluent, bioreactor, and excess activated sludge in the biological treatment and for samples taken from the photoreactor in the AOP treatment. Suspended solids (SS) and chemical oxygen demand (COD) were measured according to the standard methods (Baird et al. 2017). Total organic carbon (TOC) content was determined indirectly by the difference between the total carbon and inorganic carbon values measured by using a Formacs HT TOC/TN Analyzer (Skalar Analytical BV, Breda, Netherlands).

Conductivity and pH of the samples were measured with a conductivity meter Crison CM 35 and a pH meter Crison pH 25, respectively.

The analytical method used for the quantification of the target CEC in samples was carried out by high-performance liquid chromatography with a triple-quadrupole mass spectrometry detector. Samples were first conditioned before the analysis. First, they were filtered through a 1.2-μm glass fiber membrane filter. To extract the dissolved fraction of the target compounds from the samples, permeate was treated by solid phase extraction. It was acidified to a pH of 2 and percolated through Oasis HLB SPE cartridges at a constant flow rate. Then, the elution of the pharmaceuticals was carried out with methanol. On the other hand, to extract the solid fraction of the target compounds from the samples, the retentate was treated by sonication. The solid fraction was previously lyophilized in a Cryodos-50 lyophilizer and then extracted with methanol acidified with 5% of acetic acid. After being sonicated for 10 min and centrifuged for another 20 min at 4000 rpm, supernatants were treated by dispersive solid-phase extraction using C18 sorbent. Then, the resultant aliquot was submitted at a centrifugation for 10 min at 4000 rpm and the organic phase containing the pharmaceuticals was separated. Once they were extracted, both fractions were evaporated using a nitrogen stream and the resultant residue was dissolved in 0.3 mL of methanol:water (50:50, v/v), filtered through a 0.22-μm nylon filter and immediately analyzed by liquid chromatography-triple quadrupole mass spectrometry.

The validation of the analytical method was based in the determination of the extraction process recovery, precision, linearity, and limits of detection and quantitation (LOD and LOQ, respectively), shown in Table 9. Extraction process recovery was calculated by the difference of the peak areas of the analyte in the samples spiked before and after extraction (solutions A and B, respectively): R (%) = (A/B) × 100. The precision of the method was evaluated as repeatability in terms of relative standard deviation (RSD) of the concentrations determined in a spiked sample measured in triplicate. Linearity of the method was estimated by analyzing standard solutions in triplicate at different concentration levels in the range of concentrations expected after extraction. LOD and LOQ limits were determined as the concentrations corresponding to a signal-to-noise ratio of 3:1 and 10:1, respectively.

Table 9. Recovery, precision, linearity, limit of detection (LOD) and limit of quantitation (LOQ) for the target compounds in wastewater and sludge samples

Wastewater samples

Compound	Recovery (%)	Precision (%)	Linearity (r^2)	LOD (μg/L)	LOQ (μg/L)
Ibuprofen	89	10.0	0.994	0.012	0.039
Carbamazepine	120	2.9	0.999	0.001	0.002
Ciprofloxacin	91	4.8	0.997	0.15	0.730

Sludge samples

Compound	Recovery (%)	Precision (%)	Linearity (r^2)	LOD (μg/kg)	LOQ (μg/kg)
Ibuprofen	59	19.0	0.998	1.41	4.54
Carbamazepine	69	10.0	0.999	0.10	0.25
Ciprofloxacin	89	6.1	0.999	13.20	69.10

3.4. CEC degradation capacity of the combined treatment

Biological CEC degradation capacity in the first part of the combined treatment was evaluated through the calculation of the biological degradation rate (BDR) for each compound. This parameter estimates the rate at which the target compounds are degraded in the biological system. Making a mass balance for the system, it has for each compound

$$Q_{in} \cdot C_{in} = Q_{pe} \cdot C_{pe} + Q_w \cdot C_w + V \cdot \frac{dC_{BR}}{dt} + BDR \cdot X \quad (1)$$

Samples were taken after the dilution time, so considering that there were no changes in the concentration of the contaminants in the bioreactor, the BDR was calculated according to the equation

$$BDR = \frac{1}{X} \cdot \left(Q_{in} \cdot C_{in} - Q_{pe} \cdot C_{pe} - Q_w \cdot C_w\right) \quad (2)$$

As can be seen in Eq. (2), the rate at which target compounds will be biologically degraded depends, on the one hand, on the concentration of pharmaceuticals in the influent (C_{in}), and on the other hand on the operational parameters of the plant: HRT (as Q_{pe}), MLSS (X), and consequently SRT (as Q_w).

CEC degradation capacity by physicochemical methods in the second part of the combined treatment was evaluated through the estimation of the physicochemical degradation rate (PDR) from the adjustment of the experimental results to a pseudo–first order kinetic. The pseudo–first order kinetic model is widely accepted for interpreting the mechanism of

degradation of micropollutants in the light-driven H_2O_2/UV/AOP (Kim et al. 2009; Shu et al. 2013; Giannakis et al. 2015; Shu et al. 2016)

$$C_{ef} = C_{pe} \cdot e^{PDR \cdot t} + C_{eq} \cdot (1 - e^{PDR \cdot t}) \quad (3)$$

The rate at which target compounds will be physicochemically degraded depends, on the one hand, on the concentration of pharmaceuticals in the influent (C_{in}) and, on the other hand, on the operational parameters of the plant: peroxide dosage and the irradiance level of the lamp source.

3.5. Statistical analysis

A multivariate regression model based on the pseudo–first order kinetic was created by using the software Statgraphics Centurion XVI. It sought to express the PDR of each pharmaceutical as a function of its initial concentration and the peroxide dosage added to a photoreactor with a power supply of 150 W emitting in an UV range above 190 nm. The other complementary parameter to the PDR in the pseudo–first order kinetic model, the equilibrium concentration (C_{eq}), was also modeled as a function of both operative variables to complete the kinetic model.

4. Results and discussion

4.1. Biological degradation of pharmaceuticals in MBR stage

The concentration of the pharmaceuticals in the influent and the effluent of the MBR system are shown in Table 8. During the first doping, no ciprofloxacin was detected in the effluent, so its removal can be considered complete. Furthermore, an average removal of 66.23 ± 29.71 % and 90.04 ± 11.41 % was obtained for carbamazepine and ibuprofen, respectively. The wide variability in the percentage of removal presented by both pharmaceuticals is because the concentration of pharmaceuticals found in the effluent during the 3 days of doping was uneven. This was due to the instability produced by the impact that the sudden addition of pharmaceuticals had on the system because of the lack of adaptation of the biomass to such xenobiotic compounds (Taheran et al. 2016). It is not surprising that the removal efficiencies obtained for the tested pharmaceuticals varied in a large range and in different ways because they are hydrophilic compounds and possess diverse molecular structures and functional groups, which will condition their behavior in the biological process (Tadkaew et al. 2011).

Observing the data of concentration of pharmaceuticals taken from the excess sludge (Table 10), it can be appreciated that part of the pharmaceuticals accumulated in the sludge instead of being degraded biologically. The analysis of the sludge taken from the MBR during the first doping revealed that ciprofloxacin was the pharmaceutical that

accumulated more in the sludge (2024.84 ± 670.52 μg/kg). As a consequence, its removal was due in 8.87 ± 1.49 % to its accumulation onto the sludge, whereas the remaining 91.13 ± 1.49 % was due to a biological degradation. In contrast, ibuprofen did not accumulate in the sludge, so it is deduced that its removal was completely due to its biodegradation. The low removal observed for carbamazepine, which was the most persistent compound (66.23 ± 29.71 %), was due in part to sorption into the sludge, but mostly by biodegradation (98.72 ± 0.34 %).

Table 10. Concentration of carbamazepine, ciprofloxacin and ibuprofen in the sludge and biological degradation rate in the MBR stage

	Carbamazepine	
Doping	Excess sludge μg/kg	BDR [μg/(h·mgMLSS)]
1	739.52 ± 331.36	0.37 ± 0.16
2	18272.69 ± 10927.13	5.19 ± 0.21
3	47928.57 ± 2211.28	31.22 ± 3.36

	Ciprofloxacin	
Doping	Excess sludge μg/kg	BDR [μg/(h·mgMLSS)]
1	2024.84 ± 670.52	0.05 ± 0.00
2	8461.55 ± 4671.63	0.53 ± 0.03
3	25110.61 ± 5223.34	2.91 ± 0.30

	Ibuprofen	
Doping	Excess sludge μg/kg	BDR [μg/(h·mgMLSS)]
1	0.00 ± 0.00	0.50 ± 0.06
2	6456.69 ± 3544.58	5.43 ± 0.21
3	10892.50 ± 2692.94	31.40 ± 3.42

These results are consistent with the framework proposed by Wijekoon et al. (2013). Because ibuprofen is a very hydrophilic compound, logD = 0.14 (Scholar SciFinder 2018), and the functional groups associated with its molecular structure are the electron-donating type (EDG), it was completely biodegraded and therefore nothing was accumulated in the sludge. So, according to the Eq. (2), an experimental BDR of 0.50 ± 0.06 μg/(h·mgMLSS) was obtained for ibuprofen during this doping (Table 10). On the opposite side, the sorption of the carbamazepine, which is also a hydrophilic compound (logD < 3.2) but with a moderate hydrophobicity, logD = 1.89 (Scholar SciFinder 2018), was more favored (739.52 ± 331.36 μg/kg). However, the presence of a strong electron-withdrawing group (EWG) in its molecular structure makes it a more persistent compound. Therefore, the low removal efficiency of the carbamazepine observed during the first doping can be attributed to a lower BDR [0.37 ± 0.16 μg/(h·mgMLSS)]. Between the two extremes, the removal of the hydrophilic compounds containing both EWG and EDG, as ciprofloxacin, logD = − 0.35 (Scholar SciFinder 2018), will depend on the type of their functional groups. In the concrete case of ciprofloxacin, it is reported that this pharmaceutical is a compound with a strong sorption trend to sludge (Cecconet et al. 2017), which is consistent with the high accumulation of this pharmaceutical in the sludge observed in this research (2024.84 ± 670.52 μg/kg). As a consequence, the lowest BDR was observed for this pharmaceutical, 0.05 ± 0.00 μg/(h·mgMLSS).

These results are consistent with those found in the literature. Removal of ibuprofen above 90% in MBR systems is usually reported (Sipma et al. 2010). Trinh et al. (2016) obtained an almost complete removal of ibuprofen (> 95 %) from wastewater, almost entirely due to the biodegradation of this pharmaceutical, which is in accordance with the results obtained in the current study. Better results were obtained by Kim et al., reporting in their study a complete removal of ibuprofen from wastewater, with 99 % removed by biodegradation, whereas the remaining 1 % of the removal was due to sorption into the sludge (Kim et al. 2014). Similar results have been observed in previous studies for removal of ciprofloxacin in MBR. Park et al. observed a removal of 94.2 % of this compound in a full-scale MBR (Park et al. 2017). They also performed a lab-scale MBR to know the mechanism of removal of this compound, among others. They obtained removals ranging between 76 % and 95 %, and the results demonstrated that the removal of this compound was mainly due to a strong sorption onto the biosolids, complemented by biodegradation (Park et al. 2017). In the case of the carbamazepine, a better removal was obtained compared to the results typically observed in the literature (Cecconet et al. 2017). The higher removal obtained could be because of the existence of nitrification and denitrification processes. Because the MBR used in this study possessed an anoxic zone with a predenitrification configuration with high internal recirculation and SRT to remove nitrogen, a better removal of carbamazepine, a nitrogenbearing compound, was achieved, such as Hai et al. observed in their study (Hai et al. 2011). They noticed previously that a MBR operating in anoxic-aerobic conditions enhanced the removal of

carbamazepine. Wijekoon et al. also achieved a high removal of carbamazepine in their study (58%) using a MBR inoculated with sludge from a nutrient removal bioreactor from a full-scale WWTP. They observed that the removal was due to its biodegradation to a larger extent, and to a lesser extent, but not least, because of accumulation in the sludge (Wijekoon et al. 2013), which is in good agreement with the results obtained in the current study.

The concentration of pharmaceuticals during the next two dopings presented a higher stability, especially as the system was reestablished and adapted to the presence of these pollutants. When increasing the concentration of pharmaceuticals in the influent in Dopings 2 and 3, it can be observed in Table 10 that the BDRs obtained in these dopings were higher with respect to the first doping, which agrees with the work of Alvarino et al., in which they affirmed that the biodegradation of organic micropollutants depends on the concentration at which they are present in the water (Alvarino et al. 2018). As can be also observed, the presence of pharmaceuticals in the sludge also increased as a consequence of their accumulation. However, the higher inlet concentration exceeded the capacity of removal of the system by both routes. This led to a higher amounts of pharmaceuticals escaping through the influent, as can be seen in Table 8. This resulted in removals of 88.36 % ± 0.75 % (of which 99.05 ± 0.84 % was due to biodegradation) for carbamazepine, 93.12 ± 0.96% (of which 96.60 ± 1.85 % was due to biodegradation) for ciprofloxacin, and 92.28 ± 2.11 % (of which 99.48 ± 0.29 % was due to biodegradation) for ibuprofen in

Doping 2 and removals of 96.18 ± 0.19 % (of which 99.58 ± 0.39 % was due to biodegradation) for carbamazepine, 90.63 ± 0.77 % (of which 98.13 ± 0.53 % was due to biodegradation) for ciprofloxacin, and 96.48 ± 0.33 % (of which 99.84 ± 0.03 % was due to biodegradation) for ibuprofen in Doping 3.

To know the experimental biodegradability of tested pharmaceuticals in a MBR operating at 4250 mg MLSS/L and HRT of 16 h, regardless of their initial concentration, the values of BDR were fitted against their concentration in the influent. The data fit well to a linear model ($R^2 > 0.998$), getting for each pollutant the BDR as a function of its initial concentration. Carbamazepine and ibuprofen presented the same biodegradability {6.2×10^{-3} $\mu g/[(\mu g/L)_{in} \cdot h \cdot mgMLSS]$}, whereas ciprofloxacin showed a lower degradation value {5.8×10^{-3} $\mu g/[(\mu g/L)_{in} \cdot h \cdot mgMLSS]$}. It confirms the earlier comments that although ciprofloxacin was removed more easily than carbamazepine and ibuprofen from water, its biodegradability is lower than those of the other two. Ibuprofen showed the highest BDR among the three pharmaceuticals tested, consistent with its greater biodegradability compared to the others, as previously reported by Kim et al. (2014).

4.2. Physicochemical degradation of pharmaceuticals in AOP stage

With the aim of physicochemically degrading the pharmaceuticals that could not be removed in the biological process, samples from the effluent of the MBR system were subsequently treated by AOP in the photoreactor. The results, expressed as a degradation percentage of the pharmaceuticals with

respect to the concentration in the biological effluent, are shown in Figure 10.

The effluent taken from the biological process during the first doping, which contained 45.4 μg/L of carbamazepine and 7.47 μg/L of ibuprofen (ciprofloxacin was completely biodegraded in the MBR), was treated with 25, 50 and 100 mg/L of hydrogen peroxide in the photoreactor (a, b and c respectively in Figure 10), obtaining in all the cases the same result. As can be observed, no pharmaceuticals remained in the effluent after 10 min of treatment for whatever peroxide dosage tested.

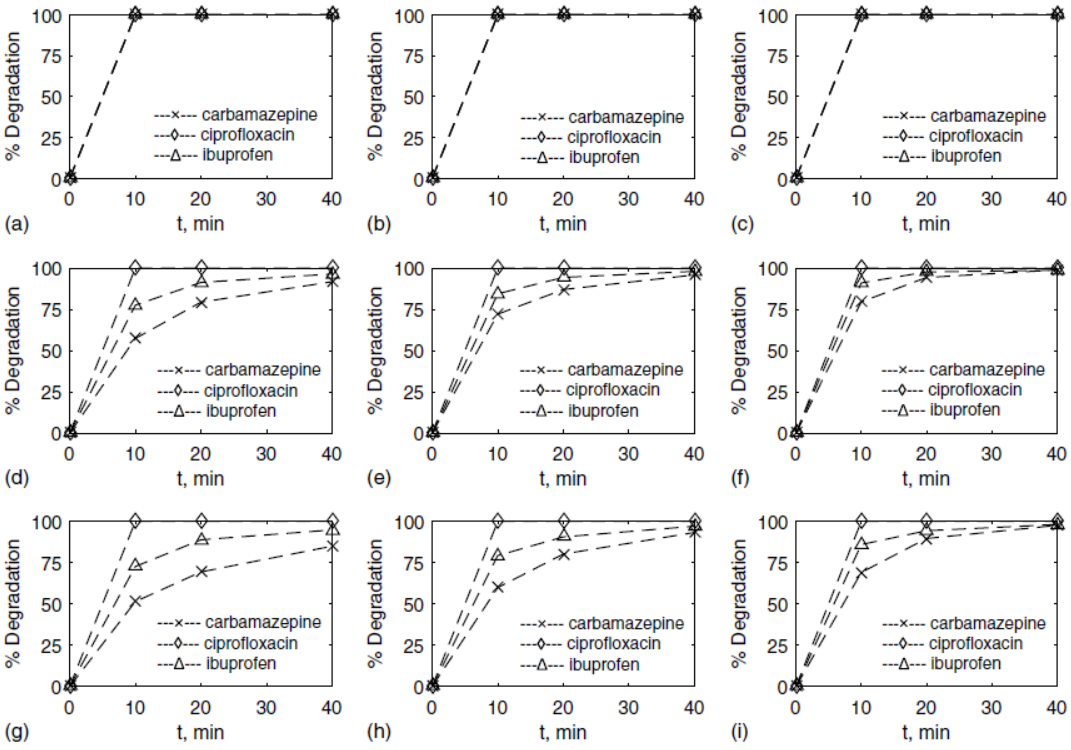

Figure 10. Experimental degradation efficiencies obtained for carbamazepine, ciprofloxacin and ibuprofen during the treatment of dopings 1 (a, b, c); 2 (d, e, f) and 3 (g, h, i) under 25 mg/L (a, d, g), 50 mg/L (b, e, h) and 100 mg/L (c, f, i) of oxidant. Trends are represented by a broken line.

A higher concentration of the pharmaceuticals was detected in the biological effluent taken during the second doping (116.33, 7.48 and 76.07 μg/L of carbamazepine, ciprofloxacin, and ibuprofen, respectively). In this case, the treatment by using AOP did not result in a complete degradation of all of them. The treatment of the biological effluent with 25 mg/L of peroxide (Figure 10d) resulted in a degradation of ibuprofen that ranged from 77.52 % at 10 min to the 96.46 % observed after 40 min. The lowest degradation was shown for carbamazepine, whose degradation ranged from 57.36 % to 91.75 % after 40 min. The dosage of 25 mg/L was enough to completely degrade ciprofloxacin. As can be observed in Figure 10 e and f, the addition of higher concentrations of peroxide (50 and 100 mg/L respectively) improved the degradation of the pharmaceuticals that were not completely removed using 25 mg/L of peroxide. Ibuprofen presented degradations between 84.45 % at 10 min and 98.04 % at 40 min using 50 mg/L of peroxide, and between 90.99 % and 98.67 % at the same time with 100 mg/L of oxidant. As for carbamazepine, its degradation changed from 72.11 % at 10 min to 95.89 % after 40 min when using 50 mg/L of peroxide, and its degradation was even higher when 100 mg/L of oxidant was added (from the 79.56 % obtained at 10 min to 98.96 % after 40 min).

The lowest degradation percentages were obtained when treating the biological effluent during the third doping, where 189.33 μg/L of carbamazepine, 43.83 μg/L of ciprofloxacin, and 157.67 μg/L of ibuprofen were detected in the effluent of the biological stage. Among them, carbamazepine was again the pharmaceutical that presented the worst

degradation. Its degradation yield was only 51.41 % with 10 min of treatment using 25 mg/L of peroxide, but 85.00 % degradation was achieved when the treatment was extended to a total of 40 min. These yields were significantly improved when higher peroxide concentrations were added (from 59.91 % to 93.30 % and from 69.05 % to 97.60 % when adding 50 and 100 mg/L, respectively). Ciprofloxacin, by contrast, was completely degraded again before the first 10 min regardless of the peroxide dosage added. As for ibuprofen, it showed a degradation of 72.67 % at 10 min of treatment, which was increased to 94.82 % when prolonging the treatment to 40 min. Just as occurred with the carbamazepine, the degradation of ibuprofen increased substantially with the dosage of peroxide, increasing from the 72.67 % obtained with 25 mg/L in 10 min, to 79.32 % and 85.98 % when using 50 and 100 mg/L, respectively. The increment of the yields associated with the higher degradation rate provided by the addition of higher peroxide dosages was less accentuated at 40 min because it was compensated for by a longer time of treatment (as occurred with the carbamazepine). The best degradation for ibuprofen was obtained using 100 mg/L of peroxide and 40 min of treatment (98.14 %).

The degradation of these pharmaceuticals in real urban wastewater effluents using light-driven H_2O_2/UV AOP without any previous changes in its pH has been investigated only by a few authors. In the study of De la Cruz et al., an effluent from the secondary settler of a WWTP was treated without altering the properties of the wastewater (pH of 7.42 and 15.93 mg/L TOC) by H_2O_2/UV AOP using 50 mg/L of peroxide to degrade 32 CECs that

were not removed by the conventional activated sludge process, including carbamazepine, ciprofloxacin, and ibuprofen (De la Cruz et al. 2012). With a treatment time of 10 min, they achieved a reduction in their presence by up to 75 % for carbamazepine, 69 % for ciprofloxacin, and completely for ibuprofen, whereas 30 min was enough to completely remove all of them from the water. Alfonso-Olivares et al. also investigated the treatment of a secondary effluent from an urban WWTP, which contained up to 23 different pharmaceuticals, by using the photo-assisted H_2O_2/UV AOP without modifying the physicochemical characteristics of the wastewater (pH of 7.97 and 20.42 mg/L TOC) (Afonso-Olivares et al. 2016). They obtained a complete degradation of ciprofloxacin in 5 min of treatment regardless of the peroxide dosage used, similar to what was obtained in this study. The degradation of ibuprofen ranged from 67 % to 99 % when increasing the peroxide dosage from 5 to 25 mg/L. Among the three target pharmaceuticals, carbamazepine was the hardest to degrade, as also observed in the present report. They achieved a degradation of nearly 60 % in 40 min of treatment. Data from the literature explain that carbamazepine is a compound that is harder to degrade by H_2O_2/UV AOP because it shows low degradation rates by direct photolysis, so its degradation is mainly due to the reaction with hydroxyl radicals, whereas ciprofloxacin and ibuprofen are degraded by both hydroxyl radicals and UV light (Kim et al. 2009; Giri et al. 2011; Shu et al. 2013).

The rate with which pharmaceuticals were degraded in the AOP stage was estimated by the calculation of the PDR from the adjustment to a

pseudo–first order kinetic model of the experimental data of pharmaceutical concentration in the blends taken from the photoreactor at the different time intervals. The values of the PDR obtained for each pharmaceutical in each experimental condition are shown in Table 11. The C_{eq} and the average correlation coefficient of each adjustment are also shown. As can be observed in Table 11, the adjustment of the data to the pseudo–first order kinetic model was in all cases greater than 0.99. This agrees with several reports (Shu et al. 2013, 2016), in which it is stated that the degradation of these pharmaceuticals by photo-assisted AOP follows such a kinetic.

Table 11. Physicochemical degradation rates obtained in the AOP. Ciprofloxacin is not shown because of the lack of data caused by its prompt elimination.

Doping	H_2O_2 mg/L	Carbamazepine			Ibuprofen		
		PDR min^{-1}	C_{eq} µg/L	R^2	PDR min^{-1}	C_{eq} µg/L	R^2
1	25	$107.2x10^{-2}$	0.00	≈ 1	$64.3x10^{-2}$	0.00	≈ 1
	50	$107.2x10^{-2}$	0.00	≈ 1	$64.3x10^{-2}$	0.00	≈ 1
	100	$107.2x10^{-2}$	0.00	≈ 1	$64.3x10^{-2}$	0.00	≈ 1
2	25	$9.3x10^{-2}$	6.97	≈ 1	$14.8x10^{-2}$	2.49	0.9987
	50	$12.1x10^{-2}$	3.89	0.9969	$17.1x10^{-2}$	1.41	0.9963
	100	$15.3x10^{-2}$	0.96	0.9995	$23.6x10^{-2}$	1.00	0.9989
3	25	$7.9x10^{-2}$	21.19	0.9983	$13.7x10^{-2}$	7.55	0.9996
	50	$9.3x10^{-2}$	8.33	0.9994	$14.2x10^{-2}$	4.07	0.9941
	100	$12.1x10^{-2}$	3.07	≈ 1	$17.3x10^{-2}$	2.78	0.9931

The PDR of carbamazepine and ibuprofen during the treatment of the biological effluent of the first doping was 107.2×10^{-2} and 64.3×10^{-2} min^{-1}, respectively, regardless of the peroxide dosage added, due to the fast degradation of the small amounts of these pollutants detected in the water. Lower PDRs were observed during the treatment of the biological effluent

from the second doping. Carbamazepine and ibuprofen, present in higher concentrations, were physicochemically degraded at a rate of 9.3×10^{-2} and 14.8×10^{-2} min^{-1}, respectively, when 25 mg/L of peroxide was added. The PDR of both pollutants improved with the increment of the peroxide dosage. When the biological effluent was treated with 50 mg/L of peroxide, carbamazepine showed a PDR of 12.1×10^{-2} min^{-1}, whereas ibuprofen increased its PDR to 17.1×10^{-2} min^{-1}. The PDR increased even more when 100 mg/L of peroxide was added (15.3×10^{-2} min^{-1} for carbamazepine and 23.6×10^{-2} min^{-1} for ibuprofen). In the case of the treatment of the effluent coming from the biological system during the third doping, carbamazepine and ibuprofen showed even lower PDRs according to the higher concentrations of both in the water. The PDR of carbamazepine was observed to range from 7.9×10^{-2} to 12.1×10^{-2} min^{-1} as the peroxide dosage was increased from 25 to 100 mg/L. Ibuprofen again presented a PDR higher than that of carbamazepine, ranging from 13.7×10^{-2} to 17.3×10^{-2} min^{-1} with the added dosage of peroxide. The reason the degradation rate of ciprofloxacin is not shown is because it could not be calculated due to the lack of data caused by its prompt elimination.

Experimental PDRs obtained at the different operation conditions in the AOP treatment are well consistent with those reported in other studies. Carbamazepine was degraded at a rate ranging from 7.9×10^{-2} to 107.2×10^{-2} min^{-1} (Table 11). Degradation rates included in that range have been observed in the treatment of real urban wastewater effluents containing carbamazepine by using H_2O_2/UV AOP without altering the pH.

Specifically, Kim et al. (2009) managed to degrade this contaminant at a rate of 9×10^{-2} min^{-1} with 8.2 mg/L of peroxide, whereas Giannakis et al. (2015) could degrade it at a higher rate, 64.4×10^{-2} min^{-1}, using a peroxide dosage of 25 mg/L. Furthermore, the degradation rates from 13.7×10^{-2} to 64.3×10^{-2} min^{-1} (Table 11) observed in this study in the case of ibuprofen are similar to those reported previously by Shu et al. (2013), who obtained degradation rates from 38×10^{-2} to 56×10^{-2} min^{-1} using an H_2O_2/UV AOP with peroxide dosages from 25 to 50 mg/L.

A regression model that could explain the data obtained by means of just the main effects was found for the PDRs of both contaminants. The best regression was obtained with a model in which the PDR depended linearly on the peroxide dosage and exponentially on the inverse of the concentration of the pharmaceutical in the biological effluent. The regression models obtained for the PDR of carbamazepine and ibuprofen are shown in Eqs. (4) and (5) (R^2 = 99.95 % and R^2 = 99.48%, respectively)

$$PDR_{CBZ} = 49.48x10^{-3} + 44.85x10^{-5} \cdot [H_2O_2] + \exp\left(-5.02 + \frac{227.87}{C_{pe}}\right)$$

$$PDR_{IBP} = -78.28x10^{-2} + 56.07x10^{-5} \cdot [H_2O_2] + \exp\left(-11.85x10^{-2} + \frac{3.36}{C_{pe}}\right)$$

Figure 11 (a and b) show the estimated response surfaces for PDRs of carbamazepine and ibuprofen. It can be appreciated that the PDR varies inversely proportionally to the initial concentration of the pharmaceutical, and its relationship is far stronger than it keeps with the peroxide dosage. As the concentration in the biological effluent increases, the PDR decreases

drastically. This is in accordance with Shu et al. (2013), as they postulated that it might be because the decomposition of these types of persistent pollutants generate by-products that also intervene in the oxidation process.

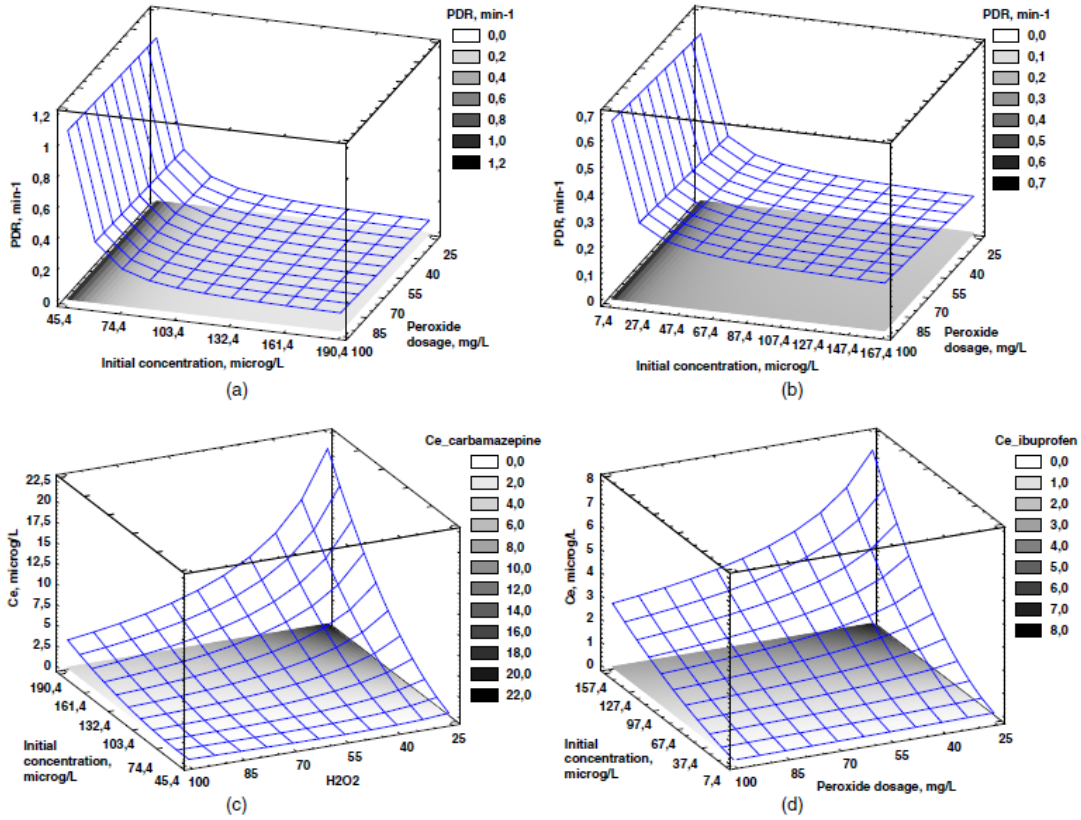

Figure 11. Estimated response surface of PDR (a and b) and Ceq (c and d) in relation to peroxide dosage and concentration in the influent for carbamazepine (a and c) and ibuprofen (b and d). Ciprofoxacin is not shown due to the lack of data caused by its prompt elimination

Moreover, the increase of the peroxide dosage only produces a slight increase in the PDR, probably because the optimum peroxide dosage for the tested conditions has been exceeded. Several studies report that a further increase in the peroxide concentration beyond the optimal dosage may cause the degradation rate to remain relatively constant or even decrease. This is due to an excess of peroxide generating a high concentration of

hydroxyl radicals in the water, which promotes the reaction of the hydroxyls with residual peroxide or even among themselves (Poyatos et al. 2010). Similar results were observed in other studies such as the degradation of a mix of 40 pharmaceuticals (Wols and Hofman-Caris 2012) or the decomposition of sulfaquinoxaline (Liao et al. 2016) by UV/H_2O_2 AOP.

By contrast, any regression model involving just the main effects was found to explain the C_{eq} data obtained. Therefore, in addition to involving the main effects, the interactions between both effects were included in the regression model (two-factor interactions model). In this way, a well-fitted regression model was obtained in which the main effect was the combination of both effects. This means that the concentration of pharmaceuticals that will remain in the effluent of the process is given by a term of interaction between both peroxide and pharmaceutical concentrations: C_{eq} is directly proportional to the squared initial concentration and inversely proportional to the peroxide dosage, as Eqs. (6) and (7) show (R^2 = 99.38 % and 99.43 %, respectively)

$$C_{eq\_CBZ} = -31.92x10^{-2} + 17.17x10^{-3} \cdot \left(\frac{{C_{pe}}^2}{H_2O_2}\right) + 96.28x10^{-4} \cdot [H_2O_2] - 18.61x10^{-3} \cdot C_{pe}$$

$$C_{eq\_IBP} = 13.96x10^{-2} + 61.61x10^{-4} \cdot \left(\frac{{C_{pe}}^2}{H_2O_2}\right) - 20.48x10^{-4} \cdot [H_2O_2] + 81.24x10^{-4} \cdot C_{pe}$$

In Figure 11 (c and d), the estimated response surfaces for C_{eq} of carbamazepine and ibuprofen are shown. In them it can be observed that

the reliance of C_{eq} on the initial concentration depends more on the peroxide dosage that is added, and vice versa. Thus, for a low peroxide dosage, C_{eq} increases drastically with the concentration of pharmaceuticals in the influent, whereas C_{eq} increases with little visible impact if the peroxide dosage is increased to 100 mg/L. In the same way, for a low concentration of pharmaceuticals in the influent, C_{eq} can even become independent of the peroxide dosage because the pharmaceutical is completely eliminated, or it can increase drastically with the reduction of the peroxide dosage if there is a high concentration of pharmaceuticals in the influent.

In the same model equation or in the estimated response surfaces in Figure 11 (c and d), it can be appreciated that C_{eq} depends to a higher extent on the concentration in the influent because this term is squared in the equation. This is because of the generation of by-products in the decomposition of the pharmaceuticals so it creates a higher competition for hydroxyl radicals in the degradation process (Shu et al. 2013). Figure 12. Observed vs predicted for the adjusted pseudo-first order kinetic model for carbamazepine (a) and ibuprofen (b). Ciprofloxacin is not shown because of the lack of data caused by its prompt elimination.Figure 12 shows the experimentally observed data versus the data estimated by the regression model.

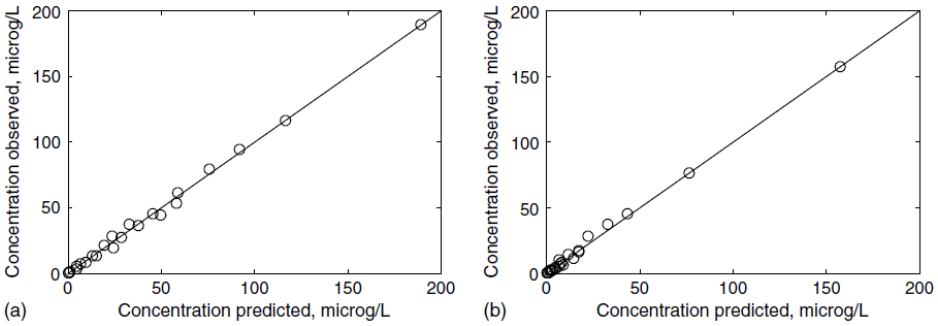

Figure 12. Observed vs predicted for the adjusted pseudo-first order kinetic model for carbamazepine (a) and ibuprofen (b). Ciprofloxacin is not shown because of the lack of data caused by its prompt elimination.

4.3. Total degradation capacity of the combined process

The global degradations of the pharmaceutical mix carried out in the combined process MBR-AOP (H_2O_2/UV) are shown in Table 12. The degradation obtained taking into account just the MBR is also shown. The removal of the tested pharmaceutical concentrations from wastewater in the MBR system was high but not complete. Thus, a further treatment is necessary to complement the degradation process of the pharmaceuticals because it is intuited that the discharge of small traces of these kinds of pollutants through the effluent of wastewater treatment plants could lead to major environmental and global health problems (Zhang et al. 2016).

As can be seen in Table 12, the coupling of a subsequent AOP treatment of 10 min with a dosage of 25 mg/L is enough to completely degrade the pharmaceuticals at the lowest tested concentrations. The concentrations normally detected in urban wastewater are lower than these (Castiglioni et al. 2006). In such a way, from 100.00 μg/L of carbamazepine present in the influent, 45.4 μg/L remained in the water after the biological degradation process, and it was not detected after the physicochemical degradation

process. Ibuprofen, which remained in the biological effluent at a concentration of 7.47 μg/L, was also completely degraded in the AOP stage. As for ciprofloxacin, it was completely removed in the bioreactor.

Table 12. Removal percentages obtained in the MBR stage and accumulated removal percentages obtained in the combined treatment for carbamazepine, ciprofloxacin and ibuprofen in each doping.

% Removal		Initial concentration (µg/L)	MBR	MBR + AOP 25 mg/L			MBR + AOP 50 mg/L			MBR + AOP 100 mg/L		
				10 min	20 min	40 min	10 min	20 min	40 min	10 min	20 min	40 min
Dop 1	Carbamazepine	100	54.60	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100
	Ciprofloxacin	10	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100
	Ibuprofen	100	92.53	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100
Dop 2	Carbamazepine	1000	88.37	95.04	97.60	99.04	96.76	98.49	99.52	97.62	99.34	99.88
	Ciprofloxacin	100	92.52	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100
	Ibuprofen	1000	92.39	98.29	99.34	99.73	98.82	99.57	99.85	99.32	99.82	99.90
Dop 3	Carbamazepine	5000	96.21	98.16	98.84	99.43	98.48	99.25	99.75	98.83	99.61	99.91
	Ciprofloxacin	500	91.23	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100
	Ibuprofen	5000	96.85	99.14	99.65	99.84	99.35	99.70	99.91	99.56	99.82	99.94

For the treatment of an influent with a concentration of pharmaceuticals 10 times higher than

usually found in urban wastewater, the complete degradation of the fraction not removed in the MBR cannot then be achieved with only 25 mg/L of peroxide in a 10-min AOP treatment. In this case, the exposure time and peroxide dosage play key roles in the AOP treatment. Obviously, the process will be more economical the less oxidant and exposure time are used. The degradation of carbamazepine obtained in the biological system, 88.37 %, is increased above 95 % after the most economic AOP treatment possible (10 min and 25 mg/L of peroxide). If tighter degradation yields are required, a degradation yield above 99 % can be obtained in 20 min using 100 mg/L of peroxide or, by extending the time exposure to 40 min, any peroxide dosage can work. Ibuprofen, with 92.39 % removal in the MBR, increased its removal yield above 99 % after 20 min of AOP treatment whatever the peroxide dosage, while ciprofloxacin, of which 92.52 % was removed in the biological stage, achieved total degradation after the AOP stage with any of the conditions tested.

Finally, when tested concentrations were more than 50 times higher than expected in urban wastewater, high removals were also obtained in the biological system, but the concentration levels in the effluent made its reuse or discharge inappropriate (189.33, 43.83, and 157.67 μg/L of carbamazepine, ciprofloxacin, and ibuprofen, respectively). For this reason, subsequent AOP treatment was totally suited. The degradation yields in this case will depend again on the removal needs that are desired, from getting 98.16 %, a complete removal, and a 99.14 % of removal for carbamazepine, ciprofloxacin, and ibuprofen, respectively, using the combined process

MBR-AOP (10 min and 25 mg/L of peroxide) to achieving an effluent of the combined process with 4.54 and 2.93 μg/L of carbamazepine and ibuprofen by employing 100 mg/L of peroxide for 40 min in the AOP stage. High peroxide dosages or exposure times or a combination of both conditions that had a high disinfection power could be justified in cases like this because in wastewaters with such high pharmaceutical and microorganism concentrations, antibiotic resistance could be promoted (Sun et al. 2016).

In a previous study, Arola et al. (2017) evaluated the removal of several CECs from real urban wastewater using a pilot-scale WWTP consisting of a MBR working at 10000 mg/L, 21 h of HRT and 33 d of SRT, and a subsequently coupled AOP treatment by pulsed corona discharge. They observed removals of 98.5 % and − 30.0 % for ibuprofen and carbamazepine, respectively, but a complete removal of both contaminants was achieved after the AOP treatment. Karaolia et al. (2017) studied the removal of various antibiotic-related CECs by a combined treatment also at a pilot scale consisting of a MBR (9 h of HRT and 30 d of SRT) with solar Fenton oxidation. With this integrated approach, they obtained a complete removal of all antibiotics except for clarithromycin, due to its low biodegradability and its high photo-persistent structural characteristics. Ouarda et al. evaluated the removal of four pharmaceutical-related CECs at concentration levels similar to those found in hospital wastewater by using the combination of MBR and an electro-oxidation process. The treatment by MBR (HRT of 18 h and 16500 mg/L of MLSS) achieved a high removal percentage for ibuprofen (≈ 90 %), whereas a low removal was obtained for

carbamazepine (≈ 10 %). However, combining the electro-oxidation process with the MBR produced a significant enhancement in the removal of the tested CECs (≈ 97 %) after 40 min of treatment (Ouarda et al. 2018).

5. Conclusions

From the results obtained with a combined treatment comprising a MBR (16 h of HRT, 13.56 d of SRT, and 4250.79 ± 495.82 mg/L of MLSS) and a subsequent AOP (H_2O_2/UV at the natural pH and 20 °C using 25, 50 and 100 mg/L of peroxide) to remove different concentrations of a mix of CECs in real urban wastewater, the following conclusions were attained:

- The removal efficiencies obtained for carbamazepine, ciprofloxacin, and ibuprofen in the biological treatment by MBR ranged from 66.23 – 96.18 %, 90.63 – 100 % and 90.04 – 96.48 %, respectively.
- The biological degradation rates observed for the tested pharmaceuticals in the biological treatment were 6.2×10^{-3} $\mu g/[(\mu g/L)_{in} \cdot h \cdot mgMLSS]$ for carbamazepine and ibuprofen and 5.8×10^{-3} $\mu g/[(\mu g/L)_{in} \cdot h \cdot mgMLSS]$ for ciprofloxacin.
- Coupling the AOP after the MBR produced a significant enhancement in the removal of CECs, achieving degradation efficiencies above 95.04 % and up to complete degradation for carbamazepine and above 98.29 % and also up to complete degradation for ibuprofen, depending on the concentration of CECs in the influent and the peroxide dosage and treatment time in the AOP. The combined system managed to complement the removal of

ciprofloxacin obtained in the MBR up to a complete removal after 10 min of AOP treatment.

- Physicochemical degradation rates from 7.9×10^{-2} to 107.2×10^{-2} min^{-1} and from 13.7×10^{-2} to 64.3×10^{-2} min^{-1} took place in the AOP stage for carbamazepine and ibuprofen, respectively. No physicochemical degradation rates were obtained for ciprofloxacin due to the lack of data caused by its prompt elimination.

Given the previous, the combination of two advanced treatment technologies such as MBR-AOP is a reliable solution for the removal of certain pharmaceuticals (carbamazepine, ciprofloxacin, and ibuprofen) present in urban wastewater, either by intrusion or discharge.

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VI - CHAPTER 3

Effect of carrier addition on water quality and pharmaceutical removal capacity of a membrane bioreactor – advanced oxidation process combined treatment.

VI - CHAPTER 3

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1. Abstract

This research was performed to assess the production of reclaimed water from urban wastewater in membrane bioreactor – advanced oxidation process (MBR-AOP) and moving bed biofilm reactor – membrane bioreactor – advanced oxidation process (MBBR-MBR-AOP) combined treatments to study the effect of biofilm incorporation. Both combined treatments were operated at the same conditions (10 h of hydraulic retention time, 6500 mg/L of mixed liquor suspended solids and 25 mg/L of hydrogen peroxide dosage over 15 min). Additionally, the removal capacity of some pharmaceuticals (carbamazepine, ciprofloxacin and ibuprofen) and their impact on the kinetic behaviour of the biomass in both systems were evaluated. From the

results, it was found a membrane-based bioreactor can achieve both wastewater secondary treatment and pre-treatment for advanced oxidation process, so both MBR-AOP and MBBR-MBR-AOP treatments have a great potential to produce high quality reclaimed water (biological oxygen demand < 0.5 mgO_2/L, suspended solids < 1 mg/L, turbidity < 1 NTU and no presence of E. coli), according to European Commission proposal 2018/0169/COD. The addition of carriers improved the biodegradation of the most persistent pharmaceuticals in the biological treatment (from 69.20 ± 1.54 to 75.14 ± 2.71 % for carbamazepine and from 60.41 ± 2.16 to 63.14 ± 2.70 % for ciprofloxacin). It had, as a consequence, the MBBR-MBR-AOP system showing a complete degradation of pharmaceuticals after 5 min AOP treatment compared to the MBR-AOP system. The loss of biomass in the MBR-AOP (from 5233.45 to 4451.92 mg/L) and the increase of the substrate degradation rate for organic matter in both treatments (from 37.27 to 41.42 and from 30.25 to 33.19 $mgO_2/(L \cdot h)$ in MBR-AOP and MBBR-MBR-AOP, respectively) are some of the consequences of pharmaceuticals in urban wastewater.

2. Introduction

Global water resources are being subjected to unsustainable pressure. The high demand for water in agriculture, responsible for 70 % of water withdrawals in the world, together with the growing demand from urban areas and industrial activity in recent years, have caused the need for sustainable water management planning (Connor et al., 2017). This fact

provides the opportunity to come over conventional wastewater management practices and adopt innovative approaches, such as using treated urban wastewater.

Treated urban wastewater reuse allows the taking advantage of an untapped resource that is valuable and abundant. Therefore, treated urban wastewater could be an important source of water supply in some areas, particularly in those arid or semiarid countries. Indeed, some countries, such as Spain or Israel, already have their own regulations for wastewater reuse in agriculture irrigation, while in many other countries it is a widely unregulated practice that reduce water scarcity and the consequent pressure on the worldwide water resources.

For this reason, the European Commission has elaborated proposal 2018/0169/COD, which aims to promote the improvement of the quality of treated urban wastewater for a responsible use in agricultural irrigation in European Union (European Commission, 2018a). In the proposal, the minimum requirements to guarantee the safety of reclaimed water were established based on the values of biological oxygen demand, suspended solids, turbidity and E. coli (European Commission, 2018b).

In addition, there are other potentially hazardous substances whose presence in reclaimed water could call into question its reuse in agricultural irrigation (European Commission, 2018b). They are the contaminants of emerging concern (CECs) and constitute another of the priority lines of water management in the European Union (European Commission, 2013).

These include contaminants such as pharmaceuticals, hormones, pesticides or personal care products. Although they are found in concentrations ranging from ng/L to μg/L, it is important to remove them from water, since they are persistent compounds that could have a significant effect to the public health or environment. Endocrine disruption, inhibition of self-purification process in water bodies or even the worrying proliferation of antibiotic resistant bacteria are some of the effects reported in literature (Hamza et al., 2016). Therefore, the European Commission also has a watch list in which substances suspected of causing damage to the environment or human health are collected and studied to make a decision about their possible regulation in water (European Commission, 2018c).

These requirements can be difficult to achieve in most of the current urban wastewater treatment plants (WWTPs) based on the conventional activated sludge (CAS) process (Arola et al., 2017). Therefore, the treatment technology in WWTPs must be updated and complemented to comply with increasingly restrictive regulations.

Membrane bioreactor (MBR) technology is a recommended alternative when remodelling the biological treatment of a WWTP is required. This technology, which relies on replacing the secondary settler in the CAS process with membrane filtration, is able to produce a high-quality effluent (Gurung et al., 2016). In addition, MBRs can significantly improve the removal of CECs with respect to the CAS process, mainly due to the proliferation of more specific microorganisms promoted by a longer solid

retention time (SRT) and the separation by membranes of CECs adsorbed in the sludge (Hamza et al., 2016).

However, it has been observed that the presence of substances, such as pharmaceuticals in urban wastewater, can affect the biological process. Biomass loss, variation of the bacterial community structures and even the affection to the organic matter and nutrients removal yields are some of the effects reported in literature (Grzes´kowiak et al., 2018; Kang et al., 2018). In this sense, the addition of plastic carriers with a similar density to water, which move freely inside the MBR has, as a consequence, a higher surface for the attachment and growth of microorganisms as biofilm, which achieve a higher robustness of the biological system against toxic substances, since the biomass is more safeguarded (Litty et al., 2015). This combined approach is called hybrid moving bed biofilm reactor – membrane bioreactor (MBBR-MBR) technology and could further improve CEC removal as a result of both suspended and attached biomass growth. However, there are not many studies that have evaluated the use of MBBR technologies for CEC removal, and especially the MBBR-MBR technology (Fernandes et al., 2018).

It should be noted that although both MBR and MBBR technologies could improve CEC removal compared to the CAS process, the low biodegradability of many of these contaminants is the reason why they do not present a high removal yield in both biological systems (Ahmed et al., 2017; Alvarino et al., 2018). Therefore, the reuse or even the discharge of treated wastewater still containing CECs is not recommended due to the consequences that this could have. In this case, when biological treatments

are not effective, the use of other physicochemical treatments, such as activated carbon or advanced oxidation processes (AOPs), are employed. In particular, light-driven AOPs are strongly recommended for CEC removal as they have demonstrated high removal yields (Rizzo et al., 2019). Light-driven AOPs, such as H_2O_2/UV AOP, are physicochemical treatments that involve the generation of powerful, nonselective radicals (generally hydroxyl radicals) by decomposition of H_2O_2 by UV light. The oxidizing power of these radicals is capable of degrading the chemical structure of practically any contaminant (Poyatos et al., 2010). Despite being one of the most effective treatments in CEC removal, high energy and reagent costs are required to compensate for the decrease in performance caused by turbidity in water (Carré et al., 2018). This is the main reason why its application as a tertiary treatment in urban WWTPs is still scarce.

An alternative to reduce these costs and make light-driven AOP viable is coupling it with other technologies. Pre-coupling MBR or MBBR-MBR technologies with a H_2O_2/UV AOP could have two decisive advantages: i) removing particles from water, reducing turbidity and therefore increasing UV light penetration and process performance; ii) removing a higher load of pollutants at the entry of the AOP process, either by biodegradation or adsorption onto the sludge and subsequent separation by membrane, thereby reducing reagent costs. Thus, remodeling urban WWTPs with the suggested combined treatment could not only improve the effluent quality for reuse according to the requirements of the proposal but also reduce or even completely remove CECs.

To the best of our knowledge, few studies have been performed concerning the combination of membrane-based bioreactors with AOP for the treatment of urban wastewater and none concerning specifically MBBR-MBR with AOP. Therefore, there is no data about how the addition of carriers could benefit the global process in relation to reclamation requirements and CEC removal (Arola et al., 2017; Karaolia et al., 2017).

In line with this, this study aimed to evaluate the employment of a combined treatment in urban WWTPs for producing reclaimed water with sufficient quality to be reused. For this purpose, fulfilling the requirements established in reuse proposal 2018/0169/COD and the removal capacity of three common CECs (namely carbamazepine, ciprofloxacin and ibuprofen) in an MBR-AOP treatment, working at 10 h of HRT and 6500 mg/L of MLSS and 25 mg/L of peroxide for 15 min, were evaluated and compared with the results obtained when adding biomass growing as biofilm in an MBBR-MBR-AOP. In addition, the impact of the tested CECs on the kinetic behaviour of the biomass in both biological processes was evaluated.

3. Material and methods

3.1. Experimental set-up

The combined treatment was continuously fed with real wastewater from the WWTP Los Vados (Granada, Spain) and consisted of a biological reactor with a photochemical reactor as tertiary treatment (Figure 13).

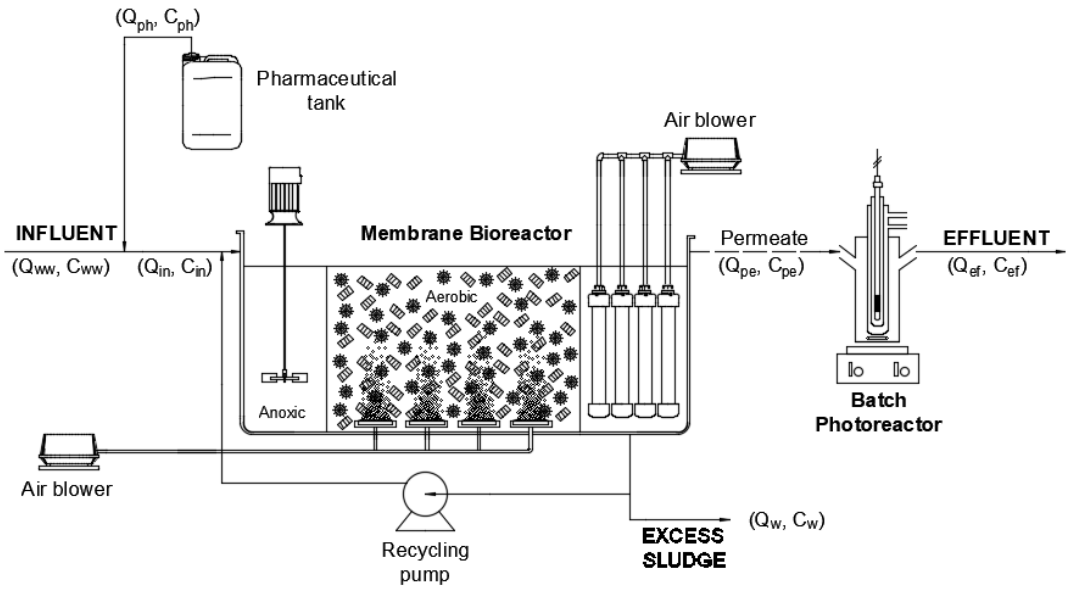

Figure 13. Pilot plant

The biological reactor was comprised two tanks, a first 272 L cylindrical tank, in which biological treatment in two anoxic and aerobic compartments was carried out, and a second 78 L rectangular tank, in which physical separation was carried out using 4 submerged hollow-fibre ultrafiltration membrane modules with a 0.04 μm nominal pore size and a 0.97 m^2 unit surface area (ZW-10, ZENON®). The biological reactor also had a compressor that intermittently supplied air to the cylindrical tank to maintain dissolved oxygen between set point levels, while a blower continuously supplied air to the rectangular tank for air scouring the membranes. In addition, a recycling pump was used to maintain the mixed liquor suspended solids (MLSS) as a constant.

The employed photochemical reactor was purchased from UV-Consulting Peschl®. It consists of a cylindrical batch reactor with a 0.8 L

working volume. A medium-pressure mercury vapour lamp with a broad emission spectrum in the UV range above 190 nm was employed as the photo-irradiance source. The lamp (150 W) was emplaced on the central axis of the reactor and was isolated by a cylindrical quartz tube, which was surrounded by a cooling jacket. The UV lamp was cooled by a thermostatic bath to keep the temperature at 20 ºC in the photoreactor. The photoreactor was equipped with mechanical stirring to maintain perfect mixing.

3.2. Operating conditions and experimental procedure

During the research, two different biological treatments were tested based on the use of membranes: conventional MBR and hybrid MBBR-MBR.

In the first experiment, the combined MBR-AOP treatment was tested. The pilot plant was operating continuously for 2 months, in which samples were taken daily from the influent, excess sludge and effluent of the MBR. Samples of effluent from the MBR were subsequently treated and analysed in the batch photoreactor. Once the performance of the combined treatment was evaluated, the pharmaceutical removal capacity of the combined treatment was evaluated during three weeks. For this purpose, a mixture of 3 pharmaceuticals was continuously added to the influent of the pilot plant, in such a way that concentrations of 100, 10 and 100 μg/L of carbamazepine, ciprofloxacin and ibuprofen, respectively, were simulated. These three pharmaceuticals were tested due to their common presence in urban wastewater and their physicochemical characteristics. Ibuprofen is an easily degradable nonsteroidal anti-inflammatory. On the other hand,

carbamazepine is a biologically persistent and non-degradable by direct photolysis, antiepileptic drug. Finally, ciprofloxacin is an antibiotic with a strong sorption trend to sludge recently added to the watch list. To ensure that the treatment of any concentration currently found in urban wastewater is covered, these concentrations were established at a value slightly higher than the maximum concentrations found in the literature for carbamazepine (18.50 μg/L), ciprofloxacin (6.45 μg/L) and ibuprofen (55.97 μg/L) in real influent of urban wastewater (Tran et al., 2018). The effects of such pharmaceuticals on the biomass of the system and on the kinetic behaviour were also studied.

Referring to the operating conditions, the dissolved oxygen setpoint in the bioreactor was maintained between 1.2 and 3 mg/L. Biological treatment was operated at 10 h of HRT and approximately 6500 mg/L of MLSS. The sludge flow of recycling was maintained at 90 L/h. All these conditions resulted in an experimental SRT of 23 days. Samples of effluent from the bioreactor were subsequently treated in the batch photoreactor by UV/H_2O_2 AOP for 15 min with 25 mg/L hydrogen peroxide. Several samples were extracted from the photoreactor at different residence times (0, 2.5, 5 and 15 min) to analyse the follow-up removal of pharmaceuticals in the process.

Once the first experiment was finished, the effect of including additional biomass as a biofilm was evaluated by incorporating carriers in the bioreactor. For this, a second experiment was carried out, in which the bioreactor was filled with AnoxKaldnes™ K1 carriers with a 35 % filling ratio, corresponding to a 175 m^2/m^3 net surface area in the reactor. In this

experiment, the hybrid MBBR-MBR-AOP system was tested at the same operation conditions in the bioreactor (resulting in 26 days of SRT) and treatment time and peroxide dosage in the photoreactor established in the first experiment.

3.3. Analytical methods

The suspended solids (SS), biological oxygen demand (BOD_5) and chemical oxygen demand (COD) measurements were carried out according to the procedures established in the Standard Methods (Baird et al., 2017). To measure the biofilm suspended solids (BFSS), a given number of carriers in a Tween 80 surfactant dispersant solution were centrifuged for 20 min at 3000 rpm. Once the biofilm was separated from the carriers, the BFSS were measured according to the determination of SS. The turbidity and colour were measured according to UNE-EN ISO 7027-1:2016 and method B of UNE-EN ISO 7887:2012, respectively. Total organic carbon (TOC) was determined by the difference between the total carbon and inorganic carbon values in water using a FormacsHT TOC/TN Analyser. Conductivity, pH and temperature were measured with a conductivity meter, Crison CM 35®, and a pH meter, Crison pH 25®, respectively. The recount of E. coli was carried out using the membrane filtration method according to Manual Difco™, based on filtration using a 0.45 μm membrane and subsequent incubation at 44 °C in plates with Endo Agar as culture medium.

3.4. Toxicity assays

The measure of toxicity is also important where AOP treatment is adopted. The high reactivity of the hydroxyl radicals or the possibility of the generation of toxic byproducts in these processes could represent a risk for reusing reclaimed water.

Only a few studies have evaluated the toxicity of the effluent after a biodegradation process using a conventional process, but none have used a combined process (Grandclément et al., 2017). The Microtox® bioassay, based on changes on the luminescence of the luminescent marine bacteria Vibrio fischeri, was employed to measure toxicity. A Microtox Model 500 toxicity analyser (Instrumentación Analítica S.A., Spain) was used to measure the toxicity of the water at the input and output of the bioreactor and the output of the photoreactor. Toxicity was expressed as Equitox/m^3 after 15 min of exposure.

3.5. Fate of pharmaceuticals in the combined treatments

The fate of the pharmaceuticals was estimated from the analysis carried out on 100 mL influent, excess sludge and effluent samples, collected daily during the doping. The analytical method used for quantifying pharmaceuticals in water and sludge samples was carried out using high-performance liquid chromatography with a triple-quadrupole mass spectrometry detector and has been validated previously in the study of

Monteoliva-García et al. (2019). Both method and associated parameters can be found in detail in their work (Monteoliva-García et al., 2019).

Knowing the pharmaceutical concentrations and the flow rates of influent, effluent and excess sludge, the fate of the pharmaceuticals was estimated by a mass balance on the biological system (Equation (1)).

$$Q_{in} \cdot C_{in} = Q_{pe} \cdot C_{pe} + Q_w \cdot C_w + V \cdot \frac{dC_{BR}}{dt} + BDR \cdot MLSS \quad (1)$$

$Q_{in} \cdot C_{in}$ is the mass load of pharmaceuticals spiked in the influent, $Q_{pe} \cdot C_{pe}$ is the fraction of pharmaceuticals that remain in the effluent and $Q_w \cdot C_w$ is the fraction removed by the excess sludge. Since samples were taken after a dilution time necessary to ensure that there were no changes in the concentration of the contaminants in the bioreactor ($V \cdot dC_{BR}/dt = 0$), the fraction of pharmaceuticals removed by biodegradation, $BDR \cdot MLSS$, can be calculated as the difference of the fractions commented previously. In addition, knowing the MLSS in the bioreactor, the rates at which the pharmaceuticals were degraded in both biological systems were also calculated from Equation (1) and compared among them.

3.6. Kinetic study

Respirometric analyses were carried out on the activated sludge samples from the MBR and MBBR-MBR systems at steady state, in order to compare the kinetic behaviour of the biomass in both wastewater treatment technologies. Furthermore, the same analyses were also carried out after

doping to study the effects derived from the presence of pharmaceuticals in urban wastewater. The respirometric experiments were carried out in a BM-Advance respirometer (Surcis S.L., Spain) (Leyva-Díaz et al., 2014; Martín-Pascual et al., 2012). The yield coefficient (Y_H), substrate degradation rate for organic matter ($r_{su,H}$) and decay coefficient (b_H) for heterotrophic biomass were evaluated.

3.7. Statistical analysis

The results obtained from the analyses were treated using statistical software, Statgraphics® Centurion XVI. An F-test was used to compare the variances of two samples while a t-test was used to compare the means. In both cases, 95.0 % confidence intervals were used.

4. Results and discussion

4.1. Influent characterisation

The total suspended solids (TSS) coming from the primary settler during experiment 1 was 105.79 ± 26.72 mg/L, of which 92.75 ± 24.00 mg/L were volatile suspended solids (VSS), while the TSS during experiment 2 was 119.47 ± 19.16 mg/L, with an average VSS of 104.47 ± 14.71 mg/L.

In terms of turbidity, the average value was around 206.99 ± 43.45 NTU in experiment 1 and 213.44 ± 53.68 NTU in experiment 2. The colour of the wastewater was measured as a function of the spectral absorption coefficient (α) at three different wavelengths: α (λ = 436), α (λ = 525) and α (λ = 620).

The results for the experiment 1 influent were 12.65 ± 2.54 m^{-1}, 9.71 ± 2.60 m^{-1} and 5.33 ± 0.88 m^{-1}, respectively, and 12.56 ± 3.35 m^{-1}, 9.16 ± 1.90 m^{-1} and 5.29 ± 1.04 m^{-1}, respectively, for the experiment 2 influent.

The pH of the influents were 7.76 ± 0.15 and 7.69 ± 0.12 during experiments 1 and 2, respectively. Regarding conductivity, the value in the influent ranged between 1023.59 ± 171.92 μS/cm during experiment 1 and between 1023.00 ± 118.62 μS/cm during experiment 2. The average influent temperature was 19.25 ± 4.77 ℃ and 19.98 ± 4.40 ℃ during experiments 1 and 2, respectively.

The organic matter contained was characterised in terms of BOD_5, COD and TOC. BOD_5, COD and TOC of the influent treated during experiment 1 were 266.36 ± 48.16 mgO_2/L, 476.99 ± 103.57 mgO_2/L and 157.34 ± 36.44 mgC/L, respectively, while those in the influent treated during experiment 2 were 266.00 ± 38.69 mgO_2/L, 489.81 ± 86.60 mgO_2/L and 163.31 ± 33.14 mgC/L.

For the microbiological count, the average number of cfu present in the influent was 6.93 ± 0.51 log(cfu/100 mL) during experiment 1 and 7.19 ± 0.65 log(cfu/100 mL) during experiment 2.

Finally, the toxicity of the influent was also measured in both experiments. The results indicated that the urban influents to the MBR system were not toxic. It can be noted that, although there are no discharge limit values for the toxicity of water treated in WWTPs, the Municipal Ordinance that regulates discharges to the Granada sewage system sets the

limit value at 25 Equitox/m^3, so water with a toxicity higher than this value was considered toxic (Granada City Council, 2010).

The statistical analysis of these parameters determined that there were no statistically significant differences between the physicochemical properties of the influents during both operating experiments (Table 13), so the observed variations were a consequence of the typical fluctuations of the pollutant load in the wastewater from the WWTP (Martín-Pascual et al., 2016). In light of this, it is important to qualify that differences in the results of this research must be only due to the addition of carriers in the MBR.

Table 13. Physicochemical characteristics of the influent

Parameters	Cycle 1 (MBR-AOP)	Cycle 2 (MBBR-MBR-AOP)
TSS, mg/L	105.79 ± 26.72	119.47 ± 19.16
FSS, mg/L	13.04 ± 4.99	15.00 ± 5.66
VSS, mg/L	92.75 ± 24.00	104.47 ± 14.71
Turbidity, NTU	206.99 ± 43.45	213.44 ±53.68
α (λ=436), m^{-1}	12.65 ± 2.54	12.56 ± 3.35
α(λ=525), m^{-1}	9.71 ± 2.60	9.16 ± 1.90
α(λ=620), m^{-1}	5.33 ± 0.88	5.29 ± 1.04
pH	7.76 ± 0.15	7.69 ± 0.12
Conductivity, µS/cm	1023.59 ± 171.92	1023.00 ± 118.62
Temperature, °C	19.25 ± 4.77	19.98 ± 4.40
BOD_5, mgO_2/L	266.36 ± 48.16	266.00 ± 38.69
COD, mgO_2/L	476.99 ± 103.57	489.81 ± 86.60
TOC, mgC/L	157.34 ± 36.44	163.31 ± 33.14
E. Coli, log(cfu/100mL)	6.93 ± 0.51	7.19 ± 0.65
Toxicity, equitox/m^3	4.03 ± 0.33	3.60 ± 0.75

4.2. Organic matter removal and kinetic characterisation of biomass

While the MBR and the hybrid MBBR-MBR were working at steady state, no statistically significant differences were observed in the physical properties of the biomass. Working with the imposed physicochemical characteristics of the influent from the urban WWTP and in the established operating conditions, the pH, conductivity and temperature of the biomass from the MBR system were 7.40 ± 0.17, 633.11 ± 60.15 μS/cm and 20.52 ± 3.55 °C respectively, while the properties of the activated sludge from the MBBR-MBR system were 7.35 ± 0.26, 659.91 ± 82.51 μS/cm and 20.16 ± 3.01 °C. The experimental mixed liquor total suspended solids (MLTSS) concentration in the activated sludge from the MBR system was 6452.36 ± 519.193 mg/L, from which 5233.45 ± 430.34 mg/L were mixed liquor volatile suspended solids (MLVSS), while 6412.84 ± 803.14 mg/L of MLTSS were maintained in the MBBR-MBR system, from which 5221.71 ± 723.78 mg/L were MLVSS. BFSS concentration growing on the carriers was 710.49 ± 87.22 mg/L.

At the kinetic level, however, statistically significant differences were observed between the kinetic behaviour of the biopopulations present in both technologies. The characteristics of the heterotrophic biomass in both systems are listed in Table 14.

Table 14. Kinetic parameters for the characterization of heterotrophic biomass

Kinetic characterization	MBR		Hybrid MBBR-MBR	
	Steady state	Doping	Steady state	Doping
Y_H (mgVSS/mgCOD)	0.60 ± 0.02	0.60 ± 0.01	0.56 ± 0.01	0.56 ± 0.01
$r_{su,H}$ (mgO_2/(L·h))	37.27 ± 2.13	41.42 ± 0.67	30.25 ± 1.30	33.19 ± 1.02
b_H (d^{-1})	0.0610 ± 0.0017	0.0527 ± 0.0011	0.0538 ± 0.0013	0.0522 ± 0.0026

The $r_{su,H}$, which is directly related to the organic matter removal capacity of the biological treatment, presented a value of 37.27 ± 2.13 $mgO_2/(L \cdot h)$ in the MBR, which is in the range of values founded in other research (Leyva-Díaz et al., 2015a, 2015b). However, the addition of carriers resulted in a decrease of such $r_{su,H}$ in the hybrid system, 30.25 ± 1.30 $mgO_2/(L \cdot h)$, which is similar to what is observed by Leyva-Díaz et al. (Leyva-Díaz et al., 2016). This is probably due to a slower mass transfer (Butler and Boltz, 2013). While in flocs, the substrate transport into the microorganism occurs through the cell wall, in the case of biofilm systems, the substrate has to first pass through the extracellular polymeric substance layer to reach the cell wall. In spite of that, the statistical analysis determined that there was no statistically significant decrease in the organic matter removal with respect to that obtained in the MBR. The reason could be that the treatment capacity of the system is higher than the contaminant load. If the $r_{su,H}$ of the MLSS is much higher than the organic matter content in the influent, a decrease of such magnitude in the $r_{su,H}$ could not significantly affect the removal yield, because the observed $r_{su,H}$ is still sufficient to degrade the organic matter content in the influent. As can be observed in Table 15, removal yields are very close to a complete removal.

Table 15. Organic matter removal yields in MBR and hybrid MBBR-MBR systems.

Technology	Phase	% BOD_5	% COD	% TOC
MBR	Steady state	96.44 ± 1.84	85.73 ± 2.79	86.02 ± 3.33
	Doping	99.01 ± 0.62	88.56 ± 2.41	90.75 ± 2.00
MBBR-MBR	Steady state	97.23 ± 1.68	87.84 ± 5.67	86.54 ± 3.99
	Doping	98.30 ± 0.46	87.42 ± 0.50	88.28 ± 0.72

The BOD_5, COD and TOC removal yields obtained in both systems agree with those obtained by other authors for similar conditions (Leyva-Díaz et al., 2017; Rodríguez et al., 2014).

On the other hand, statistically significant differences were also obtained for the Y_H and the b_H of both biopopulations, parameters closely related, at the macroscopic level, to the sludge production. The biomass from the MBR showed a Y_H of 0.60 ± 0.02 mgVSS/mgCOD and a b_H of 0.0527 ± 0.0011 d^{-1}, and both are higher than those observed for the biomass from the MBBR-MBR system, 0.56 ± 0.01 mgVSS/mgCOD and 0.0522 ± 0.0013 d^{-1}, respectively. This is in accordance with the experimental excess sludge generation in both systems. Working at the same operating conditions, the experimental excess sludge production of the MBR system was 14.35 L/d, whereas the experimental excess sludge produced by the hybrid MBBR-MBR was 12.69 L/d. Thereby, the addition of carriers had, as a result, a lower excess sludge generation, which is an advantage provided by the MBBR-MBR for two reasons. On one hand, it is because the excess sludge management is one of the main problems faced by the current WWTPs due to the high cost involved. And on the other hand, due to the fact that the fate of the excess sludge is usually as organic amendment in agriculture, the contamination of agricultural products with emerging contaminants is reduced. This is due to the fact that the excess sludge contains a high percentage of the pharmaceuticals that enter through the wastewater influent.

Once the doping was continuously added to the influent, a different biomass behaviour was observed in both MBR and MBBR-MBR technologies. Due to the presence of the pharmaceuticals in the influent, the MBR system showed a statistically significant loss of MLVSS. The concentration dropped rapidly from 5233.45 ± 430. 34 mg/L to stabilise at an average value of 4451.92 ± 297.64 mg/L. Once the biomass was stable, the b_H decreased from 0.0610 ± 0.0017 d^{-1} to 0.0527 ± 0.0011 d^{-1}, which may be due to the acquisition of antibiotic resistance by biomass. Calero-Díaz et al. (2017) also observed something similar. Doping pharmaceuticals in an MBR resulted first in an increase of the b_H from 0.0741 to 0.1116 d^{-1}, but this decreased with exposure time to 0.0933 d^{-1} (Calero-Díaz et al., 2017). Despite the lower concentration of biomass in the MBR, the organic matter removal yield in the system was not negatively affected. This seems reasonable according to the kinetic behaviour of the biomass in Table 14. The stressful situation caused by the presence of pharmaceuticals in water resulted in an increase in $r_{su,H}$ that compensated and even slightly increased the organic matter removal. In this way, removal of BOD_5, COD and TOC increased by around 3% (Table 15).

On the other hand, the MLVSS concentration remained practically constant in the hybrid system after detecting the presence of xenobiotics in water. These results are in accordance with reported literature. Biofilm systems are widely known for being little prone to changes due to the fact that biomass is more safeguarded (Litty et al., 2015). For this reason, this system proved to be very resistant to pharmaceuticals in the influent. The

results obtained from the respirometric analyses supported what occurred, since the same values of Y_H and b_H were observed before and during the doping with pharmaceuticals (Table 14). Instead, the presence of the pharmaceuticals in the hybrid system resulted in an increase in $r_{su,H}$, from 30.25 ± 1.30 $mgO_2/(L \cdot h)$ to 33.19 ± 1.02 $mgO_2/(L \cdot h)$. However, this increase had a smaller magnitude than that in the MBR, and as a consequence, the improvement in organic matter removal yields was not statistically significant (Table 15).

4.3. Quality parameters for reusing wastewater according to proposal 2018/0169/COD

As can be observed in Table 16, both MBR and MBBR-MBR were able to provide water with the best quality (type A) on their own according to 2018/0169/COD (European Commission, 2018b).

With respect to the BOD_5, as mentioned above, both biological treatments obtained similar organic matter removal yields, with BOD_5 of 6.44 ± 4.22 mgO_2/L and 6.88 ± 3.88 mgO_2/L in the effluents produced by the MBR and MBBR-MBR, respectively. These values agree with the high BOD_5 removal yields provided by membrane biological systems (Leyva-Díaz et al., 2017; Xiao et al., 2019), and they are below the limit of 10 mgO_2/L established for type A quality reclaimed water.

As for SS, both MBR and MBBR-MBR treatments also produced effluents with a concentration clearly below the more demanding

concentrations established in the proposal (European Commission, 2018b). This was mainly due to the presence of the ultrafiltration membranes in the bioreactor since they have a 0.04 μm cut-off size. The concentration of SS in the effluent was < 1 mg/L in both systems, which allows the consideration of both effluents for reuse in crops with the most demanding requirements.

The values of turbidity for the water treated in the MBR and MBBR-MBR were drastically reduced and were very close between the systems. They ranged between 0.40 ± 0.21 NTU and 0.35 ± 0.28 NTU, respectively. As happened with SS, the low and constant values were obtained independent of the biological process used, as a consequence of the filtration through the ultrafiltration membranes (Ortiz Uribe et al., 2015), which were responsible for the bulk of the total removal that took place during the biological treatment (greater than 99 %). Similar results were obtained by Mamais et al. (2017) when using an MBR-RO system for reclaiming urban wastewater. They obtained an effluent with a turbidity of 0.32 ± 0.1 NTU at the exit of the MBR that worked at 6 - 8 g/L of SS and 10 h of HRT (Mamais et al., 2017).

Table 16. Quality parameters reclaimed wastewater.

	MBR	MBR + AOP	MBBR-MBR	MBBR-MBR + AOP
BOD5 (mgO_2/L)	6.44 ± 4.22	0.3 ± 0.2	6.88 ± 3.88	0.6 ± 0.3
SS (mg/L)	< 1	< 1	< 1	< 1
Turbidity (NTU)	0.40 ± 0.21	0.34 ± 0.19	0.35 ± 0.28	0.32 ± 0.22
E. Coli (ufc/100 mL)	0.71 ±1.20	≈ 0	0.69 ± 1.11	≈ 0
$\alpha(\lambda = 436)$	1.90 ± 0.57	1.66 ± 0.59	1.86 ± 0.53	1.79 ± 0.36
$\alpha(\lambda = 525)$	1.38 ± 1.78	1.21 ± 0.83	0.74 ± 0.20	0.63 ± 0.29
$\alpha(\lambda = 620)$	0.47 ± 0.30	0.44 ± 0.32	0.43 ± 0.38	0.41 ± 0.27
Toxicity	≈ 0	≈ 0	≈ 0	≈ 0

Concerning the microbiological count of E. coli, the maximum number of cfu found in the effluent from the biological treatments was 3 cfu/100 mL, with yields above 99.99 % in both cases. Such high yields were obtained as a result of the larger size of these microorganisms in relation to the pore diameter of the membranes used, 0.04 μm (Arévalo et al., 2012). It can be noted, therefore, that the occasional presence of E. coli in the permeate was probably due to poorly practiced sampling or cross-contamination.

Another two important parameters to consider for the reuse of reclaimed wastewater, but that are not covered in the proposal, are colour and toxicity of reclaimed water, which were also measured. The colour of the wastewater was significantly reduced for all the wavelengths evaluated. The a was reduced by more than 84.68 ± 4.21 %, 91.88 ± 2.09 % and 91.70 ± 7.64 % in the MBR and 84.63 ± 5.13 %, 91.03 ± 6.09 % and 90.64 ± 6.38 % in the MBBR-MBR for wavelengths λ = 436, λ = 525 and λ = 620, respectively. Such yields are not surprising due to the excellent performance of colour removal reported for both treatments as a consequence of the degradation and ultrafiltration processes carried out in the membrane-based bioreactors. (Collivignarelli et al., 2019). In addition, both biological treatments were able to remove toxic compounds present in urban wastewater (≈ 0 equitox/m^3).

The subsequent treatment of the effluents from the MBR and the MBBR-MBR by AOP slightly improved some of the characteristics of the reclaimed water. The BOD_5 of the reclaimed water decreased to well below the strictest limit to achieve values of 0.3 ± 0.2 mgO_2/L and 0.6 ± 0.3 mgO_2/L in the MBR-AOP and MBBR-MBR-AOP, respectively. However, the

removal of SS, turbidity and colour did not significantly improve. The use of AOP after both membrane processes made it possible to ensure the total disinfection of the reclaimed water in both MBR-AOP and MBBR-MBR-AOP combined treatments thanks to the UV light and the high reactivity of the hydroxyl radicals (Carotenuto et al., 2016). Furthermore, coupling the AOP after the biological treatment did not add toxicity, so the water reclaimed in both combined treatments was not toxic at all (≈ 0 equitox/m^3). This means that no toxic byproducts were formed in the effluent and that the AOP was effectively stopped (Yuan et al., 2011).

Nevertheless, coupling both technologies had no impact on the quality type of the reclaimed water. Therefore, it could be emphasized that it does not make sense to implement an AOP after an MBR or MBBR-MBR for improving quality of the water, since these systems can achieve reclaimed water that complies with most demanding requirements of the proposal.

4.4. Removal of pharmaceuticals

However, coupling MBR and MBBR-MBR with AOP does make sense for the removal of pharmaceuticals, as can be observed in Table 17. The concentrations of target pharmaceuticals in the output of both biological and combined treatments are shown in this table.

As can be seen in Figure 14, where the different fates of the pharmaceuticals in both biological treatments are expressed as a percentage respect to the influent concentration, the different molecular structures and

Table 17. Concentration of carbamazepine, ciprofloxacin and ibuprofen in the influent and effluents

CEC (µg/L)	Influent	MBR effluent	MBR-AOP effluent			MBBR-MBR effluent	MBBR-MBR-AOP effluent		
			2.5 min	5 min	15 min		2.5 min	5 min	15 min
CBZ	100	27.66 ± 1.17	3.55 ± 0.74	0.41 ± 0.19	0.02 ± 0.02	18.64 ± 0.45	1.34 ± 0.21	~ 0	~ 0
CPX	10	0.61 ± 0.07	~ 0	~ 0	~ 0	0.08 ± 0.06	~ 0	~ 0	~ 0
IBP	100	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0

functional groups of the target pharmaceuticals led to different removal pathways (Tadkaew et al., 2011), which resulted in the different removal yields observed (Table 17).

During biological treatment by MBR, ibuprofen was totally removed from the water (Table 17). Furthermore, this removal was almost exclusively due to its biodegradation (99.67 ± 0.41 %) (Figure 14). Likewise, Kim et al. (2014) obtained a complete removal of ibuprofen, and they also observed that 99 % was as a result of its biodegradation (Kim et al., 2014). Several studies have also reported that ibuprofen is rapidly biodegraded in MBR-based wastewater treatment plants (Sipma et al., 2010). In fact, ibuprofen presented the highest BDR of the tested pharmaceuticals (0.59 ± 0.02 μg/(h·mgMLSS)), according to the mass balance in Equation (1).

The fate observed for the ciprofloxacin (Figure 14) agrees with the data reported in the literature (Cecconet et al., 2017; Gurung et al., 2019). Due to its structure, composed of both electron withdrawing and electron donating groups, this compound presented a high affinity to the sludge (Cecconet et al., 2017). From the results of the analysis carried out on the excess sludge, a large percentage was removed due to the fraction adsorbed onto the excess sludge (Figure 14). This characteristic is also an advantage in systems with high SRT, since it favours biodegradation due to a greater amount and more specificity of biomass. Consequently, 60.41 ± 2.16 % of the ciprofloxacin was removed due to degradation in the system (Figure 14). This led to an experimental 0.04 ± 0.00 μg/(h·mgMLSS) BDR and a 0.61 ± 0.07 μg/L concentration of ciprofloxacin in the effluent of the MBR (Table 17). The

removal yield achieved in this research (93.90 ± 0.68 %) is similar to that obtained in other studies. Park et al. (2017) obtained a 94 % removal for ciprofloxacin in a labscale MBR, from which 42 % was due to its biodegradation (Park et al., 2017). Gurung et al. (2019) also observed 93 % removal of ciprofloxacin in an MBR pilot plant; however, they argued that the removal was entirely due to adsorption onto the sludge (Gurung et al., 2019).

On the other side, carbamazepine was the pharmaceutical that presented the worst removal yield from water (Table 17). According to Tadkaew et al. (2011), the lower removal of carbamazepine from water in biological wastewater treatment systems is associated to a lower biodegradability caused by the presence of a strong electron withdrawing group in its molecular structure (Tadkaew et al., 2011). Research carried out by Naddeo et al., (2017) showed that an MBR working at 19 h of HRT achieved removal yields up to 55.16 % (Naddeo et al., 2017), which is consistent with that obtained in this research (Table 17). Wijekoon et al. (2013) also obtained similar removal yields for this compound (between 45 and 70 %) in an MBR working at 26 h of HRT and 7300 mg/L of MLTSS (Wijekoon et al., 2013). However, they observed that only around 26 % was a result of biodegradation, while the biodegradation observed in this research was around 69.20 ± 1.54 % (Figure 14). Therefore, it was degraded at a BDR of 0.41 ± 0.01 μg/(h·mgMLSS). The higher carbamazepine biodegradation observed in this work could be due to the higher concentration of carbamazepine used in this research (100 μg/L) compared

to that used in other works (from ng/L to μg/L). According to Alvarino et al. (2018), the concentration of micropollutant determines the type of metabolism used in its biodegradation (Alvarino et al., 2018). Therefore, carbamazepine could have been used as a substrate rather than a cosubstrate, thus presenting greater elimination by biodegradation. This could explain why carbamazepine removal in other works is much lower or even the accumulation of this pharmaceutical in the system and, therefore, has been observed in the effluent (Gurung et al., 2019).

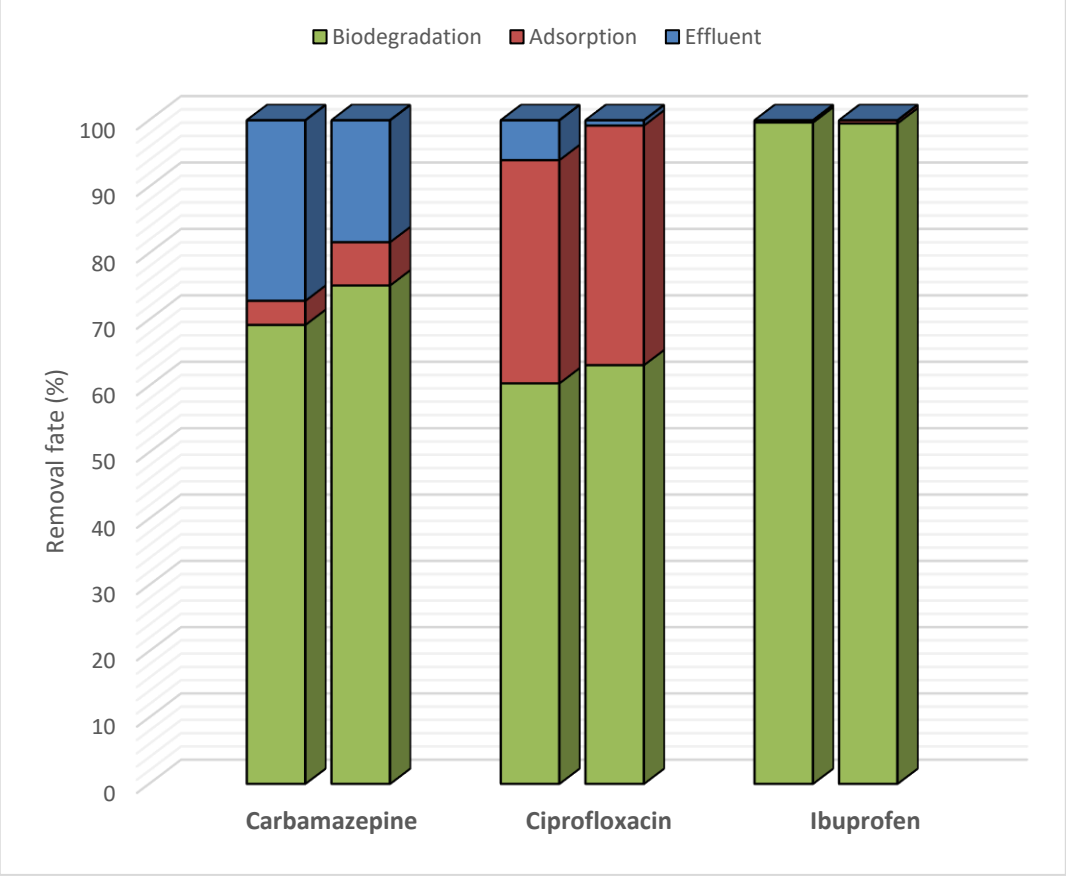

Figure 14. Fate of carbamazepine, ciprofloxacin and ibuprofen in MBR and hybrid MBBR-MBR systems

The presence of carriers in the bioreactor of the hybrid MBBR-MBR system led to some statistically significant differences in the removal of the pharmaceuticals. As Table 17 shows, the removal of pharmaceuticals in the biological system increased along general lines, probably as a result of the higher number of microorganisms and the existence of a wider variety of different microbial communities (Luo et al., 2014).

The presence of new biomass in the form of biofilm attached to the carriers and the higher SRT associated played a key role in the removal of pharmaceuticals. The BDRs of the pharmaceuticals were slower in the hybrid MBBR-MBR system compared to those in the MBR system according to the slower mass transfer in the biofilm systems (Butler and Boltz, 2013). The BDRs observed for carbamazepine, ciprofloxacin and ibuprofen in the hybrid system were 0.36 ± 0.02 μg/(h·mgMLSS), 0.03 ± 0.00 μg/(h·mgMLSS) and 0.48 ± 0.02 μg/(h·mgMLSS), respectively. However, the presence of a higher concentration of microorganisms in the bioreactor caused the fraction of biologically degraded compounds to increase (Figure 14). Therefore, the term $BDR \cdot MLSS$ (Equation (1)) in the case of the MBBR-MBR system was higher than in the case of the MBR treatment, which justifies that higher removal yields were achieved (Table 17). So, the removal of carbamazepine by biological degradation increased from the 69.20 ± 1.54 % achieved in the MBR to 75.14 ± 2.71 % in the hybrid system (Figure 14). In this way, its concentration at the inflow to the AOP treatment was reduced to 18.64 ± 0.45 μg/L (Table 17). In the case of ciprofloxacin, the percentage leaving the biological system was reduced from 5.99 ± 0.67 to 0.79 ± 0.58 % (Figure 14),

in detriment of the biodegraded and adsorbed fractions. The amount of biologically degraded ciprofloxacin increased from 60.41 ± 2.16 to 63.14 ± 2.70 %, while the fraction removed by means of the excess sludge increased from 33.60 ± 2.70 to 36.07 ± 2.70 % (Figure 14), probably as a consequence of the high biomass concentration and its strong trend to adsorb onto the sludge (Cecconet et al., 2017). Instead, the removal of ibuprofen did not present statistically significant differences compared to that obtained in the MBR system, since it was completely removed again.

Similar results have been previously reported in the literature (Jiang et al., 2018; Luo et al., 2015). The removal of pharmaceuticals in both MBR and MBBR-MBR systems were assessed and compared in a study by Luo et al. (2015). They stated that there is higher biodegradation in the hybrid system and, therefore, the removal of pharmaceuticals was higher. In particular, they observed that the removal of carbamazepine was increased by 16.2 % in the MBBR-MBR, while the removal of ibuprofen remained above 95 % in both systems (Luo et al., 2015). More recently, Jiang et al. evaluated the effect of the hydraulic retention time on the removal of some pharmaceuticals in an MBBR-MBR system. They observed an almost complete removal of ibuprofen, mostly due to its biodegradation. However, the removal of carbamazepine was 31.9 % at best, which is also a result of the higher biodegradation with respect to the adsorption (Jiang et al., 2018).

Finally, the AOP treatment of both effluents contributed to improving the total removal yield of the system, acting on the fraction of pharmaceuticals not removed in the biological system. It is important to point out that the addition of carriers in the biological system also had an indirect impact on the AOP treatment. A five minutes H_2O_2/UV/AOP treatment with 25 mg/L of hydrogen peroxide was sufficient to remove the target pharmaceuticals completely from the hybrid MBBR-MBR system effluent, while the effluent from the MBR system requires higher costs due to the necessity for higher treatment time or peroxide dosage to remove pharmaceuticals completely. Although ciprofloxacin and ibuprofen were removed completely, the high inlet concentration of carbamazepine in the biological effluent led to incomplete removal in the MBR-H_2O_2/UV combined treatment (Table 17). As of yet, there has been little research on the removal of pharmaceuticals from urban wastewater using an integrated approach combining MBR-AOP. According to Ahmed et al. (2017), integrated approaches based on combined chemical and biological treatment processes like MBR and H_2O_2/UV should be further developed (Ahmed et al., 2017). To the best of our knowledge, only Arola et al. (2017) and Karaolia et al. (2017) carried out studies similar to this one. Arola et al. (2017) studied the use of an integrated approach composed of an MBR working at 10 g/L and 21 h of HRT, with a subsequent AOP by pulsed corona oxidation for enhancing the removal of micropollutants from urban wastewater. With this combined treatment, they observed high removal yields of several micropollutants in the MBR, including ibuprofen, whereas carbamazepine showed a poor removal. However, complete removal of

both ibuprofen and carbamazepine were achieved after the AOP (Arola et al., 2017). Similarly, Karaolia et al (2017) assessed the removal of several pharmaceuticals from wastewater in an MBR - PhotoFenton pilot plant. In the same way, they completely removed all of them except the antibiotic clarithromycin due to the fact that is a very bio- and photo- persistent compound (Karaolia et al., 2017).

5. Conclusions

From the results obtained for the treatment of real urban wastewater with two combined treatments MBR-UV/H_2O_2/AOP and MBBR-MBR-UV/H_2O_2/AOP working at 10 h of HRT, 6500 mg/L of MLSS and 25 mg/L of peroxide for 15 min, the following conclusions were attained:

- The addition of carriers in the biological treatment did not produce statistically significant differences in the quality of the effluent according to the parameters established in proposal 2018/0169/COD. Both MBR-AOP and MBBR-MBR-AOP combined treatments were able to produce reclaimed water (BOD_5 < 0.5 mgO_2/L, SS < 1 mg/L, turbidity < 1 NTU and no presence of E. coli) capable of complying with the most demanding reuse requirements of proposal 2018/0169/COD, which are those established for type A quality water.
- On the contrary, the addition of carriers did have an effect on the pharmaceutical removal. BDRs were lower in the MBBR-MBR with respect to the MBR (0.36 ± 0.02 vs 0.41 ± 0.01

μg/(h·mgMLSS) for carbamazepine, 0.03 ± 0.00 vs 0.04 ± 0.00 μg/(h·mgMLSS) for ciprofloxacin and 0.48 ± 0.02 vs 0.59 ± 0.02 μg/(h·mgMLSS) for ibuprofen). However, the presence of a higher concentration of microorganisms in the MBBR-MBR due to the growth of biomass as biofilm (BFSS = 710.49 ± 87.22 mg/L) caused the fraction of compounds biologically degraded to increase from 69.20 ± 1.54 % to 75.14 ± 2.71 % for carbamazepine and from 60.41 ± 2.16 % to 63.14 ± 2.70% for ciprofloxacin. It had, as a result, a higher removal yield in the MBBR-MBR (81.36 ± 0.45, 99.20 ± 0.59 and 100 % for carbamazepine, ciprofloxacin and ibuprofen) in comparison to the MBR (72.34 ± 1.17, 93.90 ± 0.68 and 100 %). Consequently, the addition of carriers in the bioreactor can reduce the necessary treatment time in the photoreactor for CEC removal, reducing energy costs.

- Consequences derived from the presence of pharmaceuticals in the real urban wastewater included a loss of biomass (from 5233.45 ± 430.34 mg/L to 4451.92 ± 297.64 mg/L), a higher $r_{su,H}$ (from 37.27 ± 2.13 to 41.42 ± 0.67 $mgO_2/(L \cdot h)$) and a decrease of b_H (from 0.0610 ± 0.0017 to 0.0527 ± 0.0011 d^{-1}) in the MBR-AOP treatment. However, incorporating biofilms (MBBR-MBR-AOP) gave more stability to the biological system and avoided the biomass concentration in the bioreactor being affected, but did affect $r_{su,H}$ (from 30.25 ± 1.30 to 33.19 ± 1.02 $mgO_2/(L \cdot h)$).

Given the above, although the MBR is a reliable solution for reclaiming high-quality wastewater for reuse, the addition of biofilm (MBBR-MBR system) improves the stability and efficiency of the system. Moreover, for the total removal of certain pharmaceuticals (carbamazepine, ciprofloxacin and ibuprofen) at high concentrations in urban wastewater, a combination of membrane-based biological and AOP treatments is needed.

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VII - RESULTS AND DISCUSSION

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The results and partial conclusions obtained in each of the studies carried out during the experimental period of the thesis have been presented in detail in the previous chapters. Therefore, this section aims to bring together the main results obtained and discuss them jointly to extract and highlight the most valuable insights that can serve as a basis for CECs abatement and for the next-coming strategies of wastewater reuse.

1. CEC removal capacity of AOP, MBR and MBBR-MBR treatments and their combination in integrated approaches

As it has been commented throughout this document, the vast majority of the CECs are poorly removed in current WWTPs (Barbosa et al., 2016), which are usually based on the CAS biological treatment. As a consequence, the discharge of the treated water or even its reuse could constitute a serious risk to public health and the environment (Stuart et al., 2012; Helmecke et al., 2020). Therefore, alternative treatment technologies capable of adapting to the wastewater treatment conventional method and complementing it in the removal of CEC, without considerably increasing the economic and energetic costs of the process, should be investigated.

1.1. CEC removal capacity of the AOP treatment

The use of physicochemical treatments such as AOP are suitable to remove recalcitrant substances from wastewater (Rizzo et al., 2019). Therefore, a photo-assisted AOP was used as tertiary treatment to assess the removal of carbamazepine, ciprofloxacin and ibuprofen from urban wastewater using the effluent of the WWTP Granada Oeste as matrix.

Despite the fact that the removal of recalcitrant substances from water by the use of H_2O_2/UV AOP is more effective under alkaline conditions (Oturan and Aaron, 2014), the treatment of wastewater was carried out without altering this parameter because modifying the pH of large quantities of wastewater is economically unfeasible. However, the results obtained were very promising. By applying an AOP treatment with 25 mg/L of H_2O_2, concentrations of up to 59.83 μg/L of carbamazepine, 22.30 μg/L of ciprofloxacin and 54.60 μg/L of ibuprofen, which are similar to maximum concentrations currently observed in urban wastewater (Tran et al., 2018), were completely removed in less than 20 minutes. The same result was obtained in half the time (10 min) if the peroxide dosage was increased to 50 mg/L. Therefore, these results support that the complete removal of CECs at current concentration levels in urban wastewater is possible by using AOP as tertiary treatment in urban WWTPs.

Similar results were previously obtained by De la Cruz et al., who tested several AOP for CEC removal from urban wastewater. Among them,

they evaluated the removal of 32 different CECs present in the urban wastewater from a WWTP of Switzerland by the H_2O_2/UV AOP. Although they did not achieved a complete removal of every CECs, the H_2O_2/UV AOP achieved in 30 min, with 50 mg/L of H_2O_2, the complete removal of the 93.75 % of CECs from urban wastewater, among them carbamazepine, ciprofloxacin and ibuprofen were included (De la Cruz et al., 2012). As a consequence, they also showed that a near complete CEC degradation (97.01 %) can be obtained by using H_2O_2/UV AOP as tertiary treatment in urban WWTPs. More recently, Olivares et al. performed a study in which treated wastewater from an urban WWTP was spiked with 23 different CECs and treated during 45 min by H_2O_2/UV AOP in a continuous, custom-made photochemical reactor. They demonstrated in their study a minimum CEC degradation efficiency of the H_2O_2/AOP treatment of 75.8 %, which increased as the peroxide dosage increased. With a hydrogen peroxide dosage of 25 mg/L, like that used in the present study, they obtained similar results: global degradation efficiency of 98.1 % and a complete degradation for carbamazepine, ciprofloxacin and ibuprofen (Afonso-Olivares et al., 2016).

Although this is a major advance in the fight against CECs, these results can not be considered totally satisfactory, since the consumption habits existing in the present-day society are causing concentrations of CECs in urban wastewater to increase (Kim et al., 2018). Therefore, it is necessary to ensure that the removal of higher concentrations than those existing

nowadays is also possible with the aim of ensuring the capacity of response of the treatment to incoming situations.

In this sense, once the appropriate experiments were carried out, the results showed that an increase in the concentration of CECs in urban wastewater significantly reduces the removal efficiency of the AOP treatment. The treatment of wastewater with a slightly higher concentration of CECs (95.03 μg/L of carbamazepine, 17.17 μg/L of ciprofloxacin and 69.60 μg/L of ibuprofen), hereinafter referred to as doping 2, under the same operating conditions that previously managed to remove the entirety of CECs from the wastewater, i.e. a treatment time of 20 min with 25 mg/L of hydrogen peroxide, managed this time to achieve removal efficiencies of 89.50 %, 100 % and 91.52% respectively. The results were even worse when the wastewater treated in the AOP contained even higher concentrations of carbamazepine, ciprofloxacin and ibuprofen (281.00 μg/L, 98.53 μg/L and 275.00 μg/L respectively, hereinafter referred to as doping 3). Yields this time fell to 61.57 %, 100 % and 79.56 % respectively. Therefore, the growing concentration of CECs in urban wastewater would require employing more aggressive conditions, what raises the operating costs of the process.

Although there is currently not much research relating the removal performance of H_2O_2/UV AOP to the concentration of CECs in wastewater, a study conducted by Shu et al. showed that the degradation rates of CECs in the AOP decrease as their concentration in wastewater increase, resulting

in an impoverishment of the removal efficiency in the AOP treatment (Shu et al., 2013). Their results agree well with obtained in this study, which are shown graphically in Figure 15. As can be observed, the degradation rate of the CECs decreased as their concentration in the wastewater increased.

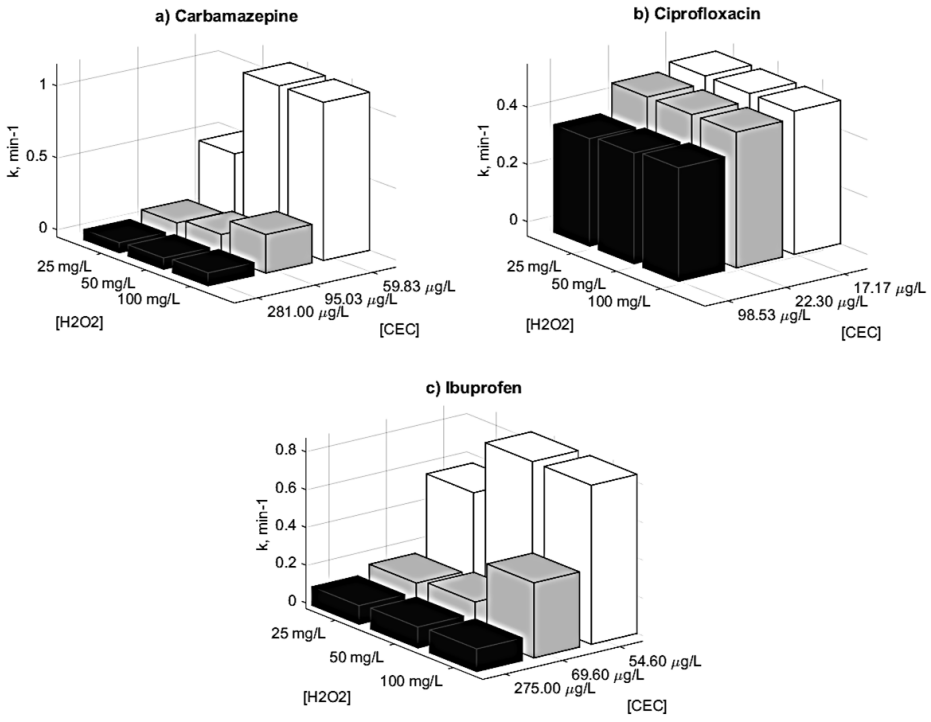

Figure 15. CEC degradation rate according to concentration in wastewater.

In order to improve the removal performance of the process in case of CECs concentrations in wastewater higher than the current ones, it was evaluated the increase of the hydrogen peroxide dosage and/or the treatment time in the photoreactor. On the one hand, the increase of the hydrogen peroxide dosage was not a great asset, as previously commented

in Chapter 1. It was noted that the higher the concentration of CECs in the wastewater, the less effect of increasing the peroxide dosage. Thus, while in doping 1 the treatment time required for complete removal of CECs was reduced by half by increasing the dosage from 25 to 50 mg/L, as above commented, the removal performance of carbamazepine, ciprofloxacin and ibuprofen in doping 2 water improved only to 93.98 %, 100 % and 94.80 % with the addition of 50 mg/L of peroxide and only up to 76.12 %, 100 % and 84.22 % in the treatment of the doping 3. Not even 100 mg/L (a dosage 4 times higher) was able to completely remove CECs from the water (98.10 %, 100 % and 100 % for doping 2 and 82.88 %, 100 % and 89.53 % for doping 3).

On the other hand, extending the treatment time in the photoreactor can also not be considered as a suitable alternative to significantly increase the performance of CEC removal. It was observed that the degradation of CECs by H_2O_2/UV/AOP follows a pseudo-first order kinetic, which agrees with other works (Pereira et al., 2007; Kim et al., 2009; Shu et al., 2013; Shu et al., 2016), characterized by a practically asymptotic tendency:

$$C = C_0 \cdot e^{k \cdot t} + C_e \cdot (1 - e^{k \cdot t})$$

As a result, removal efficiencies increased only to 97.76 %, 100 % and 96.97 % for doping 2 and 80.14 %, 100 % and 89.83 % for doping 3 by doubling the treatment time from 20 to 40 minutes, similar removal yields to those obtained when the peroxide dose was increased to 100 mg/L.

The combination at the same time of higher hydrogen peroxide doses (100 mg/L) with longer treatment times (40 min) did have a remarkable effect. In fact, a complete removal was achieved in the case of the treatment of the doping 2 and the removal yields were raised to values of 96.56 %, 100 % and 97.39 % in the treatment of the doping 3. However, this is an expensive strategy since it would trigger the economic viability of the process, since hydrogen peroxide is an expensive reagent and the ultraviolet lamps require a high energy consumption.

The addition of catalysts was also evaluated as another alternative to increase the removal efficiency of the process against a higher concentration of CECs in the wastewater, as other authors proposed in their works (Achilleos et al., 2010; De la Cruz et al., 2012). However, the results were not as expected. By one hand, the addition of 40 mg/L of Fe^{+2} to the H_2O_2/UV AOP was assessed, turning it into the process well-known as Photo-Fenton (Fe^{+2}/H_2O_2/UV AOP). The improvement in the CEC degradation with respect to the uncatalyzed process was insufficient to justify its use. In fact, the Photo-Fenton AOP showed no statistically significant improvement over the H_2O_2/UV/AOP. In a study performed by Klamerth et al., they proposed that wastewater with low organic matter content can not be treated by Photo-Fenton at neutral pH due to the fact that the absence of dissolved organic matter prevents the catalyzed reaction takes place (Klamerth et al., 2013), and in absence of acidic pH, the addition of the catalyst does not improve the performance of the H_2O_2/AOP. By other hand, the Heterogeneous

Photocatalysis ($TiO_2/H_2O_2/UV$) was tested with 1 g/L of TiO_2. Far from increasing the degradation of CECs, the addition of TiO_2 as a catalyst produced removal yields losses of to 19.18 % (carbamazepine), 4.12 % (ciprofloxacin) and 15.95 % (ibuprofen) respect to the uncatalyzed process. Other similar studies argued that such efficiency loss could be due to a light screening caused by a high presence of TiO_2 particles (Carabin et al., 2015; Jallouli et al., 2018). It is well-known that overdosing the photocatalyst load may led to a slower degradation (Rodriguez-Narvaez et al., 2017).

1.2. CEC removal capacity of the MBR treatment

The modification of a CAS bioreactor into a MBR is a straightforward process and can be carried out by incorporating ultrafiltration membranes in the secondary clarifier or any other tank of the WWTP (Castelo-Grande et al., 2010). Apart from achieving higher quality of the effluent with respect to the CAS process (Poyatos et al., 2008), this transformation could significantly improve the CEC removal capacity of the WWTP due to three main reasons: i) an improvement of the biodegradation capacity of the system as a consequence of a higher MLSS concentration, ii) the adsorption of CECs onto the sludge and subsequent separation by membranes and iii) the growth of more specific microorganisms in the degradation of certain contaminants as a result of higher SRTs (Wijekoon et al., 2013; Hamza et al., 2016; Taheran et al., 2016).

The results obtained when treating urban wastewater containing 100 μg/L of carbamazepine, 10 μg/L of ciprofloxacin and 100 μg/L of ibuprofen by MBR technology working at two differents operating condicitions (16 h of HRT and 4250.79 mg/L of MLSS; and 10 h of HRT and 6500 mg/L of MLSS) confirmed a high removal of CECs by this techonology.

Analyzing the results working at 16 h of HRT, 13.56 d of SRT and 4250.79 ± 495.82 mg/L, the MBR achieved removal yields of 66.23 ± 29.71 % for carbamazepine, 90.04 ± 11.41% for ibuprofen and a complete removal for ciprofloxacin. The different degree of removal observed among CECs is due to the fact that they possess diverse molecular structures and functional groups, what condition their fate in the biological process (Tadkaew et al., 2011). Therefore, to clarify the behavior of the CECs in the MBR, the mechanism of removal of each pharmaceutical was also studied.

In this sense, a high biodegradability was observed for ibuprofen, whose removal (90.04 ± 11.41 %) was exclusively due to biological degradation processes. Previous MBR studies also reported that similar high removal efficiencies for ibuprofen are due to a high biodegradation. In a similar study, Phan et al. obtained a removal above 90 % for ibuprofen by an anoxic-aerobic MBR, and they also reported that was exclusively due to biodegradation (Phan et al., 2014). Kim et al. assessed the removal of CECs in a full-scale urban MBR WWTP and they observed a complete removal of ibuprofen, from which 99 % was due to its biodegradation, and only 1 %

was due via adsorption onto the sludge (Kim et al., 2014). In another evaluation of the fate and removal of CECss in full-scale MBRs, Trinh et al. reported a removal yield almost complete for ibuprofen, with a contribution higher than 96 % via biodegradation (Trinh et al., 2016). As a consequence, the relative rate at which it was biodegraded in the biological system in the present study was 5.00 ± 0.57 μg/((μgin/L)·h·gMLSS).

In the same line, ciprofloxacin was biologically degraded at a similar relative rate of 5.03 ± 0.08 μg/((μgin/L)·h·gMLSS). However, it also exhibited high removal by sludge adsorption and subsequent membrane separation (8.87 ± 1.49 %), making it the only CEC completely removed in the biological process. Other authors have also attributed to ciprofloxacin a high sludge adsorption capacity. By one hand, Park et al. observed a removal of practically 100 % when analyzed the fate of ciprofloxacin at a full-scale urban MBR WWTP. They attributed this removal to a slightly higher removal via adsorption (23 %) in comparison with the present study (Park et al., 2017). However, Kim et al. by other hand reported a much higher adsorption capacity of the ciprofloxacin. They observed in their study that the removal of 89 % found for ciprofloxacin in a full-scale MBR was almost completely (98 %) due to the adsorption onto the sludge (Kim et al., 2014).

At last, carbamazepine had the worst removal performance as a result of its lower biodegradability (relative BDR = 3.71 ± 0.16 μg/((μgin/L)·h·gMLSS)) and low sludge adsorption capacity. Therefore,

about 32.18 ± 28.32 % of the carbamazepine entering the bioreactor found its fate in the effluent flow. Generally, most studies report even much lower removal yields in MBR studies (Kim et al., 2014; Phan et al., 2014; Park et al., 2017). However, according to Hai et al., a MBR operating in anoxic-aerobic conditions, as occurs in this case, leads to the development of nitrification-denitrification processes and enhances the removal of carbamazepine, a nitrogen-bearing compound (Hai et al., 2011). By this way, Wijekoon et al also obtained in their study a high removal of carbamazepine in an MBR (58 %), similar to that obtained in this work. They also reported that about two-thirds of the removal was due to biodegradation, while one-third was due to accumulation in the sludge (Wijekoon et al., 2013). Furthermore, the higher removal yield obtained in the present work could be also due to the higher concentration tested in comparison to other studies, which could contribute to the metabolization as can be seen below.

The removal yields in the MBR that worked at 6500 mg/L of MLSS and 10 h of HRT were in line with those obtained with the MBR operating at 4250 mg/L of MLSS and 16 of HRT, as can be observed in Figure 16. Carbamazepine and ibuprofen showed higher removal yields (72.34 ± 1.17 % and 100 % respectively) as a consequence of the improvement of the biodegradability, which could have been caused by longer SRT (23.02 d vs 13.56 d). However, no conclusions can be drawn since the conditions of HRT between the two experiments were different. In fact, a study of pharmaceutical removal at different combinations of HRT and SRT may

provide interesting results on the removal of CECs from wastewater and clarify why ciprofloxacin nevertheless presented a lower removal performance (93.90 ± 0.68 %) as a result of a decrease in the biodegradation.

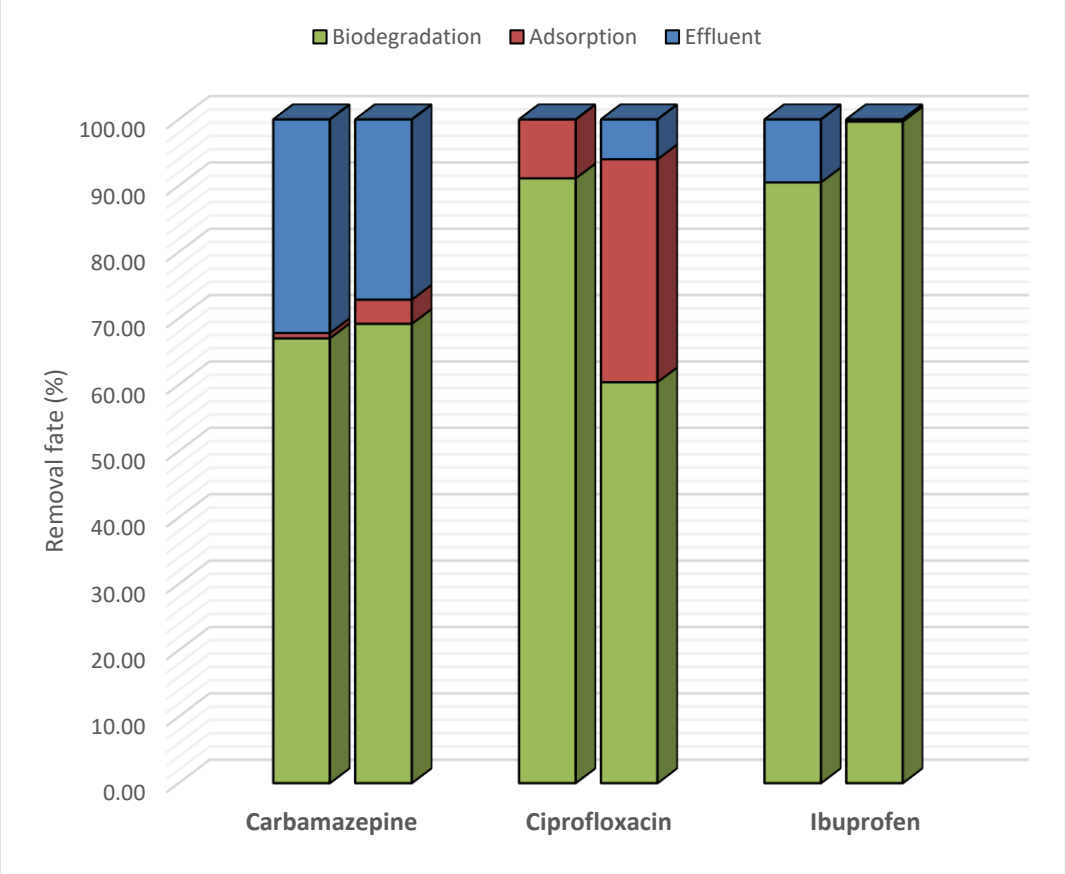

Figure 16. Removal fates in MBR treatments working at 6500 mg/L of MLSS and 10 h of HRT (Chapter 2) and 4250 mg/L of MLSS and 16 h of HRT (Chapter 3).

Specifically, the biomass present in the biological system degraded ibuprofen at a rate of 5.93 ± 0.17 μg/((μgin/L)·h·gMLSS), the highest observed, which classifies it as the most biodegradable compound. Several studies have also previously reported that ibuprofen is easibily biodegraded

in MBR treatments (Sipma et al., 2010). As a result, 99.67 ± 0.41 % of the ibuprofen concentration was degraded biologically.

As anticipated in Chapter 2, ciprofloxacin again showed a high removal rate through the excess sludge (33.60 ± 2.70 %), thereby evidencing its trend to adsorpt onto the activated sludge floc (Cecconet et al., 2017; Gurung et al., 2019). However, the degradation by biological route continued to be the main route of removal from wastewater, degrading in the MBR at a BDR of 3.59 ± 0.14 μg/((μgin/L)·h·gMLSS).

For its part, carbamazepine was the compound that suffered the worst removal in the biological system. Although it had a higher BDR than ciprofloxacin (4.12 ± 0.12 μg/((μgin/L)·h·gMLSS)), its worst adsorption capacity onto the sludge had as a result a lower removal (72.34 ± 1.17 %).

By other hand, the response of the MBR treatment to a higher concentration of CECs in the urban wastewater was also assessed. Treatment of urban wastewater with concentrations of carbamazepine, ciprofloxacin and ibuprofen 10 to 50 times higher resulted in removal efficiencies of the system above 95.04 %, 100 % and 98.29 % for carbamazepine, ciprofloxacin and ibuprofen respectively.

The increased concentration of CECs in the wastewater caused an improvement of the biodegradation capacity of the system, as it can be seen

in Figure 17, where the fate of the CECs in the biological system is represented at different concentrations of CECs in the wastewater influent.

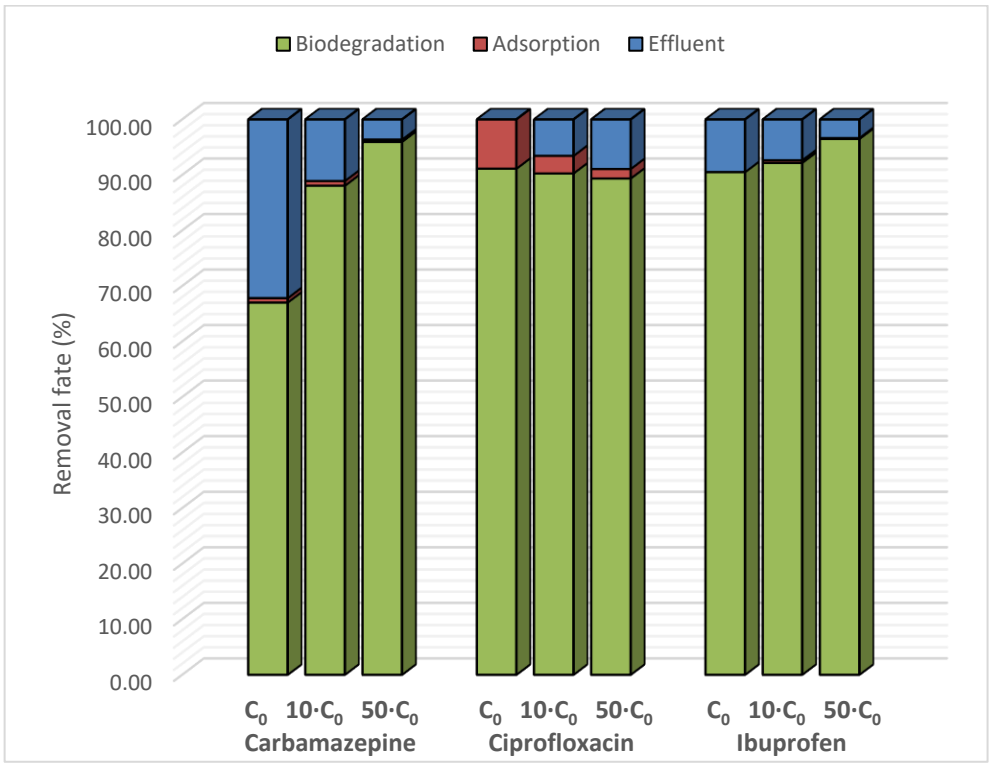

Figure 17. Effect of the CEC concentration on removal fates for carbamazepine, ciprofloxacin and ibuprofen in the MBR treatment.

This agrees with studies of Alvarino et al. and Tran et al., where they reported that the biodegradation of organic micropollutants depends on the concentration at which they are present in urban wastewater. The biodegradation of CECs appears to take place via co-metabolism rather than the metabolism pathway, since many of them are toxic/resistant to microorganisms and often are present in wastewater at trace levels. However, a higher availability of these compounds in wastewater may led

to a modification of the metabolism of certain microorganisms, even going so far as to use these pharmaceuticals as a primary substrate (Alvarino et al., 2018; Tran et al., 2018).

Specifically, carbamazepine showed the higher enhancement of the relative BDR, increasing its value from 3.71 ± 1.57 to 6.24 ± 0.67 μg/((μgin/L)·h·gMLSS). As a consequence, it became even more biodegradable than ciprofloxacin when concentrations of carbamazepine in wastewater were 5000 μg/L. Ibuprofen presented the highest BDR (6.28 ± 0.68 μg/((μgin/L)·h·gMLSS), while ciprofloxacin becomes the least biodegraded compound at high concentrations: its BDR changed from 5.03 ± 0.08 to 5.81 ± 0.60 μg/((μgin/L)·h·gMLSS).

Consequently, the enhancement of the biodegradation capacity led to higher removal yields in the MBR for carbamazepine and ibuprofen (96.18 ± 0.19 % and 96.48 ± 0.33 % respectively), but not for ciprofloxacin (90.63 ± 0.77 %), whose removal yield was negatively affected due to a decrease in the removal via adsorption, maybe due to a higher saturation of the sludge because of the higher concentration.

1.3. CEC removal capacity of the MBBR-MBR treatment

Although there are not many studies that have evaluated the use of MBBR technologies for CEC removal, and especially the MBBR-MBR technology (Fernandes et al., 2018), this technology could also present

advantages like a further enhancement of the CEC removal capacity as a result of both suspended and attached biomass growth.

The effect of carrier addition on the pharmaceutical removal capacity of the MBR technology was of great relevance. The incorporation of a moving bed (AnoxKaldnes™ K1 carriers with a 35% filling ratio) in a MBR operating at 10 h of HRT, 6500 mg/L of MLSS improved the biodegradation of the most persistent pharmaceuticals, which contributed to improving their removal performance in the combined treatment (Figure 18). Although the relative rates at which CECs were biodegraded were lower than that observed in the MBR system (3.64 ± 0.19 μg/((μgin/L)·h·gMLSS), 3.06 ± 0.20 μg/((μgin/L)·h·gMLSS) and 4.82 ± 0.20 μg/((μgin/L)·h·gMLSS) respectively), as a consequence of a slower mass tranfer in biofilm processes (Butler and Boltz, 2013), the MLSS concentration in the MBBR-MBR system was high due to the attached biomass and the absence of a suspended biomass loss (6933.80 ± 273.15 mg/L vs 5651.52 ± 178.55 mg/L), so the CEC biodegradation capacity increased. Concretely, carbamazepine increased its removal via biodegradation from 69.20 ± 1.54 % to 75.14 ± 2.71 %, while the removal of ciprofloxacin by biological way increased from 60.41 ± 2.16 % to 63.14 ± 2.70 % (Figure 18).

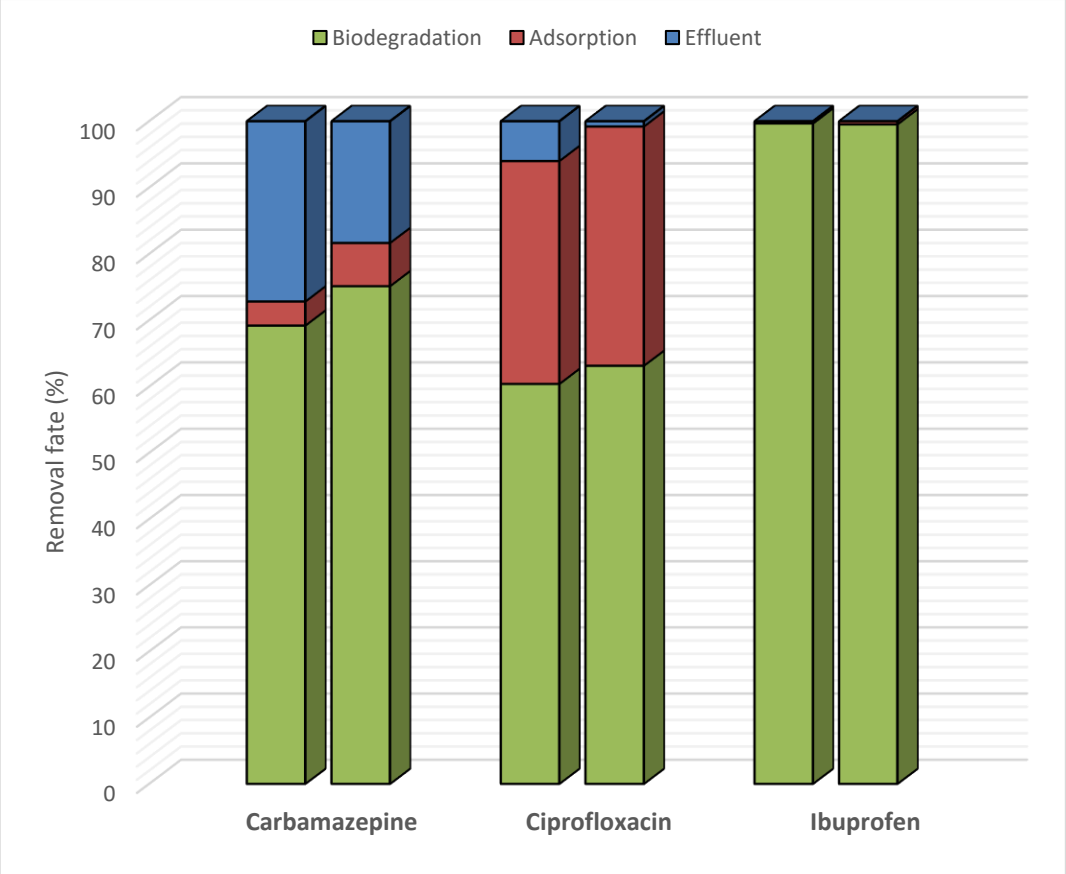

Figure 18. Fate of carbamazepine, ciprofloxacin and ibuprofen in MBR and hybrid MBBR-MBR systems

As a result, the MBBR-MBR showed CEC removal yields for carbamazepine of 81.36 ± 0.45 %, for ciprofloxacin of 99.20 ± 0.59 % and for ibuprofen of 100 %, which were higher than those obtained by the MBR at the same operational conditions (72.34 ± 1.17, 93.90 ± 0.68 and 100 %). These results agree with those published in a work carried out by Luo et al. in 2015, in which they demonstrated that, in the same operating conditions, there is a higher biodegradation in an MBBR-MBR in comparison to an MBR, and therefore, the removal of pharmaceuticals in the first one is higher.

Specifically, they observed that the removal of carbamazepine was 16.2 % higher in the MBBR-MBR, while the removal of ibuprofen remained above 95 % in both systems (Luo et al., 2015).

1.4. CEC removal capacity of the membrane-based – AOP combined treatment

An integrated approach combining membrane-based secondary treatment and AOP as tertiary treatment could be the solution to remove CECs in WWTPs. The secondary treatment could, by on hand, remove particles from water by membranes and therefore increase UV light penetration and efficiency in the AOP. While on the other hand, it could reduce the concentration of CECs at the entry of the tertiary treatment, and therefore the necessary treatment time and reagent dosages, thus reducing the costs of more aggressive treatment conditions in the photoreactor.

Results obtained in the present work confirm this integrated approach as a reliable solution for CEC removal in urban WWTPs. The combination of an MBR working at 16 h of HRT and 4250.79 mg/L with 10 minutes of AOP treatment using 25 mg/L of H_2O_2 managed to completely remove higher concentrations of carbamazepine, ciprofloxacin and ibuprofen than those usually observed in urban wastewater (100 μg/L, 10 μg/L and 100 μg/L respectively).

By other hand, the same combined treatment but with different operation conditions in the biological treatment (10 h of HRT and 6500 mg/L of MLSS) did not completely remove the tested pharmaceuticals, although its removal yield was above 99.99 %, only 0.2 μg/L of carbamazepine were detected in the effluent.

However, as a consequence of the high biodegradation obtained in the MBBR-MBR, the MBBR-MBR-AOP combined treatment also achieved a complete degradation of pharmaceuticals, but in this ocassion it only took 5 min of AOP treatment. Therefore, the addition of plastic carriers into an MBR-AOP system could reduce the energetic and chemical requirements of the AOP treatment, which could lead to significant savings in the operation of the WWTP.

Furthermore, the integrated approach showed a high potential to remove increasing concentrations of CEC in wastewater. Using the membrane-based-AOP combined treatment, it was not possible to completely remove 10-50 times higher concentrations of carbamazepine, ciprofloxacin and ibuprofen, but achieved a global removal yield above 96.82 %. It is therefore worth noting that not only is it sufficient to improve the treatment technologies of WWTPs, but that joint action must be taken to ensure that the concentrations of CECs in wastewater do not continue to grow uncontrollably, making appropriate use of pharmaceuticals, imposing restrictions on the use of pesticides, etc. and in general, all those compounds

that may pose a potential danger to the environment and human beings (European Commission, 2016).

Few authors have evaluated the use of integrated approaches combining chemical and biological treatment processes to remove CECs in urban WWTPs, so integrated approaches such as MBR-AOP should be further developed (Ahmed et al., 2017). One of them have been Arola et al. (2017), who studied the use of a combination of MBR (10 g/L and 21 h of HRT) with a subsequent AOP to remove micropollutants from urban wastewater. They observed that the treatment by AOP of the effluent from the MBR achieved a complete removal of both ibuprofen and carbamazepine (Arola et al., 2017). In the same line, Karaolia et al (2017) assessed the removal of several pharmaceuticals from wastewater in an MBR - PhotoFenton pilot plant, achieving an almost-complete removal of CECs from wastewater (Karaolia et al., 2017).

Finally, an observation that is also worth noting is that there was no increase in the rate at which the CECs were physicochemically degraded in the photoreactor after the membrane-based secondary treatment ($7.9x10^{-2}$ - $107.2x10^{-2}$ min^{-1} for carbamazepine and $13.7\ x10^{-2}$ - $64.3x10^{-2}$ min^{-1} for ibuprofen) compared to the PDRs observed during the treatment of the effluent from the CAS secondary treatment of WWTP Granada Oeste ($6.1\ x10^{-2}$ - $109.9\ x10^{-2}$ min^{-1} and $9.89\ x10^{-2}$ - $84.23\ x10^{-2}$ min^{-1} respectively). Initially it was thought that the effluent quality provided by the MBR could improve

the PDR of the CECs in the AOP treatment. However, the PDRs in both cases were very similar, and the variations observed could rather be due to other characteristics of the wastewater as pH, dissolved organic matter, etc. (Villegas-Guzman et al., 2015).

2. Quality of the reaclaimed wastewater by the membrane-based – AOP combined treatment

Both MBR-AOP and MBBR-MBR-AOP combined treatments demonstrated to be able to produce very high quality reclaimed water (BOD_5 < 0.5 mgO_2/L, suspended solids < 1 mg/L, turbidity < 1 NTU and no presence of E. coli), complying with the most demanding quality requirements established in the European Commission proposal 2018/0169/COD (BOD_5 < 10 mgO_2/L, suspended solids < 10 mg/L, turbidity < 5 NTU and E. coli < 10 CFU) (European Commission, 2018). Although there is still no literature that has evaluated the capacity to regenerate wastewater according to the European proposal, other authors have already demonstrated the excellent capacity of these combined systems for the removal of organic matter and suspended solids (Rodríguez et al., 2014; Leyva-Díaz et al., 2017).

Furthermore, other important parameters for wastewater reuse not covered in the proposal such as the colour of the water or its toxicity were also investigated with excellent results. The colour of the reclaimed water

was reduced between 84.63 and 91.88 % compared to that of the influent wastewater. Furthermore, it can be highlighted that the ecotoxicity of reclaimed water was null, which means that its reuse or discharge does not represent any potential risk to humans or the environment due to the possible presence of hydroxyl radicals or toxic byproducts in the water derived of the AOP (Yuan et al., 2011; Grandclément et al., 2017).

3. Stability of the membrane-based – AOP combined treatment

Several works have demonstrated that the presence of substances such as pharmaceuticals in urban wastewater can affect the biological process from a WWTP, with consequences like biomass lossess, variations of the bacterial community structures and even the affection to the organic matter and nutrients removal yields (Grzes´kowiak et al., 2018; Kang et al., 2018).

Regarding the response of the biological system to the presence of CECs, a series of statistically significant differences were observed both at macroscopic and microscopic level in the response between the treatment that included carriers in the bioreactor (MBBR-MBR-AOP) and the one that did not (MBR-AOP).

While the MBBR-MBR system did not suffer alterations at the macroscopic level with the presence of CECs in the wastewater, the MBR system suffered an important loss of biomass, which is a fact previously observed by other authors (Calero-Díaz et al., 2017). The MLVSS in the MBR

decreased from 5233.45 ± 430 to 4451.92 ± 297.64 mg/L. However, far from negatively impacting the removal of organic matter in the MBR, the removal rates increased from 96.44 ± 1.84 % to 99.01 ± 0.62 %, from 85.73 ± 2.79 % to 88.56 ± 2.41% and from 86.02 ± 3.33 % to 90.75 ± 2.00 % for BOD_5, COD and TOC respectively.

At microscopic level, respirometric tests showed alterations in the kinetic behaviour of the biomass in both bioreactors. The stressful situation caused by the presence of pharmaceuticals in wastewater resulted in an increase of the $r_{su,H}$ in both biological systems, maybe to provide energy reserves while the situation lasts. However, this increase was to a lesser extent in the case of the MBBR-MBR, since biofilm systems are little prone to changes as a consequence of the fact that the biomass is less exposed to the xenobiotics (Litty et al., 2015). Concretely, the $r_{su,H}$ in the MBR increased from 37.27 ± 2.13 to 41.42 ± 0.67 $mgO_2/(L \cdot h)$, while the rate reached in the MBBR-MBR was 33.19 ± 1.02 $mgO_2/(L \cdot h)$. This would justify the increased organic matter removal rates in the MBR system above commented, as previously observed Calero et al. in their study (Calero-Díaz et al., 2017). Referring to b_H, the presence of pharmaceuticals resulted in a decrease of the b_H from 0.0610 ± 0.0017 d^{-1} to 0.0527 ± 0.0011 d^{-1} once the MBR system was stabilized, reaching a b_H similar to that of the biomass in the MBBR-MBR, which remained unchanged (0.0522 ± 0.0026 d^{-1}). In the same way that the higher biomass exposure to the pharmaceuticals in the MBR led to a higher biomass loss or $r_{su,H}$, the higher contact with the pharmaceuticals also led to

the acquisition of a higher antibiotic resistance by biomass (Calero-Díaz et al., 2017). On the other hand, Y_H in both reactors remained intact despite the presence of pharmaceuticals in the wastewater (0.60 ± 0.01 mgVSS/mgCOD in the MBR and 0.56 ± 0.01 mgVSS/mgCOD in the MBBR-MBR).

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VIII - CONCLUSIONS

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The main conclusions obtained in this research are presented below in a synthesized form, in accordance with the established objectives:

- The degradation rate of carbamazepine, ciprofloxacin and ibuprofen by H_2O_2/UV AOP follows a pseudo-first order kinetics, which is strongly dependent on their initial concentration, and to a lesser extent, on the peroxide dosage. The observed degradation rates were between 6.1 $x10^{-2}$ and 109.9 $x10^{-2}$ min^{-1} for carbamazepine, between 37.59 $x10^{-2}$ y 50.02 $x10^{-2}$ min^{-1} for ciprofloxacin and between 9.89 $x10^{-2}$ and 84.23 $x10^{-2}$ min^{-1} for ibuprofen, resulting in the complete removal of up to 59.83 μg/L of carbamazepine, 98.53 μg/L of ciprofloxacin and 54.60 μg/L of ibuprofen The addition of Fe^{+2} (40 mg/L) and TiO_2 (1 g/L) catalysts to the H_2O_2/UV process fails to improve the removal performance of the process.
- The treatment of wastewater containing 100 μg/L carbamazepine, 10 μg/L of ciprofloxacin and 100 μg/L of ibuprofen by using MBR achieved removal yields of 66.23 %, 100 % and 90.04 % of these CECs when operated at 16h of HRT and around 4250 mg/L of MLSS, while the removal yields of

these contaminants were 72.34 %, 93.90 % and 100 % when the operating conditions were 10 h HRT and around 6500 mg/L MLSS. The removal was mainly due to two routes. Biological degradation was the main route, accounting for 67.01 - 69.20 % of the removal of carbamazepine, 60.41 - 91.13 % of ciprofloxacin, and 90.51 - 99.67 % of ibuprofen. However, this was not the only removal route, as up to 3.64 % of carbamazepine, 33.60 % of ciprofloxacin and 0.33 % of ibuprofen from the inffluent were removed by adsorption onto the sludge and subsequent separation by membranes.

- The MBR-AOP combined treatment working at 10 h of HRT, around 6500 mg/L of MLSS and 15 min with 25 mg/L of peroxide was able to remove over 99.99 % of the CEC concentration in an urban wastewater containing 100 μg/L of carbamazepine, 10 μg/L of ciprofloxacin and 100 μg/L of ibuprofen, while the MBR-AOP combined treatment working at 16 h of HRT, around 4250 mg/L of MLSS and 10 min with 25 mg/L of peroxide was able to remove completely those concentrations, higher than those usually observed in urban wastewater.
- The MBR-AOP combined treatment produces high-quality reclaimed wastewater (BOD_5 < 0.5 mgO_2/L, SS < 1 mg/L, turbidity < 1 NTU and no presence of E. coli) capable of

complying the most demanding quality requirements of the 2018/0169/COD proposal for urban wastewater reuse in the European Union (BOD_5 < 10 mgO_2/L, SS < 10 mg/L, turbidity < 5 NTU and E. coli < 10 cfu/100mL).

- The addition of carriers to the MBR-AOP does not improve the quality of the reclaimed wastewater due to the fact that the combined treatment already meets the highest requirements for reuse. However, it is able to increase the performance of CEC removal, being able to reduce the treatment time of the AOP to 5 min to obtain a reclaimed wastewater without CECs. In addition, the presence of carriers in the bioreactor provides the system a higher inertness, whose biomass is less exposed to the effects of xenobiotic agents. Thus, while the exposure to CECs caused a loss of biomass from 5233.45 ± 430.34 mg/L to 4451.92 ± 297.64 mg/L in the MBR-AOP system, the incorporation of carriers slowed down this loss in the MBBR-MBR-AOP. In neither case the presence of CECs in wastewater had a negative effect on the organic matter removal.

In view of the results obtained, the combination of membrane-based biological treatments with AOP is a reliable solution to regenerate high quality urban wastewater for its use in agriculture according to the proposal of Directive 2018/0169/COD, and for its reuse in general.

IX - CONCLUSIONES

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A continuación se presentan de forma sintetizada las principales conclusiones obtenidas en el presente trabajo de investigación, de acuerdo con los objetivos establecidos:

- La velocidad de degradación de carbamacepina, ciprofloxacina e ibuprofeno mediante H_2O_2/UV AOP sigue una cinética de pseudo-primer orden, la cual es fuertemente dependiente de su concentración inicial, y en menor medida, de la dosis de H_2O_2. Las velocidades de degradación observadas fueron de entre 6.1 $x10^{-2}$ y 109.9 $x10^{-2}$ min^{-1} para la carbamacepina, entre 37.59 $x10^{-2}$ y 50.02 $x10^{-2}$ min^{-1} para ciprofloxacina y entre 9.89 $x10^{-2}$ y 84.23 $x10^{-2}$ min^{-1} para el ibuprofeno, dando lugar a la completa eliminación de hasta 59.83 μg/L de carbamacepina, 98.53 μg/L de ciprofloxacina y 54.60 μg/L de ibuprofeno. La adición de catalizadores Fe^{+2} (40 mg/L) o TiO_2 (1 g/L) al H_2O_2/UV AOP no tuvo una mejora en los rendimientos de eliminación del proceso.
- El tratamiento por MBR de un agua residual con 100 μg/L de carbamacepina, 10 μg/L de ciprofloxacina y 100 μg/L de ibuprofeno consiguió eliminar el 66.23 %, el 100 % y el 90.04 %

de dichos CECs cuando operó a 16 h de HRT y en torno a 4250 mg/L de MLSS, mientras que el rendimiento de eliminación de estos mismos contaminantes fue del 72.34 %, 93.90 % y 100 % cuando las condiciones de operación fueron HRT de 10 horas y MLSS en torno a 6500 mg/L. Dichos rendimientos se debieron principalmente a dos rutas. La degradación por vía biológica supuso la principal vía de eliminación, representando el 67.01 – 69.20 % de la eliminación de la carbamacepina, el 60.41 – 91.13 % de la ciprofloxacina, y el 90.51 – 99.67 % del ibuprofeno. Sin embargo, ésta no fue la única vía de eliminación, ya que hasta un 3.64 % de la carbamacepina, 33.60 % de la ciprofloxacina y 0.33 % del ibuprofeno del agua de entrada eran eliminados mediante adsorción al fango y posterior separación por las membranas.

- El tratamiento combinado MBR-AOP con 10 h de HRT, en torno a 6500 mg/L de MLSS y 15 min con 25 mg/L de peróxido fue capaz de eliminar por encima del 99.99 % de la concentración de CECs en un agua residual urbana conteniendo 100 μg/L de carbamacepina, 10 μg/L de ciprofloxacina y 100 μg/L de ibuprofeno, mientras que el tratamiento combinado MBR-AOP (16 h de HRT, en torno a 4250 mg/L de MLSS y 10 min con 25 mg/L de peróxido) fue capaz de eliminar completamente dichas

concentraciones, más altas que las habitualmente observadas en las aguas residuales urbanas.

- El tratamiento combinado MBR-AOP produce agua regenerada (BOD_5 < 0.5 mgO_2/L, SS < 1 mg/L, turbidity < 1 NTU and no presence of E. coli) capaz de cumplir con los requisitos de calidad más exigentes de la propuesta 2018/0169/COD de reutilización de las aguas residuales urbanas en la Unión Europea (BOD_5 < 10 mgO_2/L, SS < 10 mg/L, turbidity < 5 NTU and E. coli < 10 cfu/100mL).
- La adición de soportes al tratamiento combinado MBR-AOP no mejora la calidad del agua regenerada debido a que el tratamiento combinadoya cumple con los requerimientos más exigentes de reutilización. Sin embargo, es capaz de aumentar el rendimiento de eliminación de los CECs, siendo capaz de reducir el tiempo de tratamiento del AOP hasta 5 min para obtener un agua regenerada libre de CECs. Además, la presencia de soportes en el biorreactor dotó de una mayor inercia al sistema, cuya biomasa se ve menos expuesta a los efectos de agentes xenobióticos. Así, mientras que la exposición a los CECs provocó una pérdida de biomasa desde 5233.45 ± 430.34 mg/L hasta 4451.92 ± 297.64 mg/L en el sistema MBR-AOP, la incorporación de soportes frenó dicha pérdida en el MBBR-MBR-AOP. En ninguno de los dos casos la presencia de

CECs en el agua residual supuso una afección negativa al proceso de eliminación de materia orgánica.

A la vista de los resultados obtenidos, la combinación de tratamientos biológicos basados en membranas con AOP es una adecuada solución para regenerar agua residual urbana de alta calidad para su aprovechamiento en agricultura según la propuesta de directiva 2018/0169/COD, y para su reutilización en general.

X - FUTURE RESEARCH LINES

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In line with the results presented in this work, a series of research lines are proposed, which could contribute to improving the removal of CECs from urban wastewater, and therefore, to improving the quality of reclaimed water that encourages its reuse:

- Study of CECs removal under different HRTs and SRTs to optimize biological secondary treatment and thus reduce costs of the physico-chemical tertiary treatment.
- Analysis of the operational and implementation costs of the combined treatment MBR-AOP.
- Study of CECs removal in the sludge line.
- Study of other CECs, whether other pharmaceuticals or other substances of emerging concern such as pesticides, personal care and hygiene products, etc.

XI – FUTURAS LÍNEAS DE INVESTIGACIÓN

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En línea con los resultados presentados en el presente trabajo, se propone una serie de líneas de investigación que podrían contribuir a la mejora de la eliminación de contaminantes emergentes de las aguas residuales urbanas, y por ende, a la mejora de la calidad del agua regenerada que incentive su reutilización:

- Estudio de la eliminación de CECs bajo distintos HRT y SRT para optimizar el tratamiento biológico y reducir consecuentemente los costes del proceso físico-químico.
- Análisis de los costes operativos y de implantación del tratamiento combinado MBR-AOP.
- Estudio de la eliminación de CECs en la línea de fangos.
- Estudio de otros CECs, ya sean otros fármacos u otro tipo de sustancias de preocupación emergente como pesticidas, productos de cuidado e higiene personal, etc.

ABBREVIATIONS

- AOP: advanced oxidation process
- BFSS: biofilm suspended solids
- BDR: biological degradation rate
- BOD_5: biological oxygen demand at 5th day
- CAS: conventional activated sludge
- CBZ: carbamazepine
- CEC: contaminant of emerging concern
- CFU: colony-forming unit
- COD: chemical oxygen demand
- CPX: ciprofloxacin
- DO: disolved oxygen
- EDAR: estación depuradora de aguas residuals
- EDG: electron-donating group
- EU: European Union
- EWG: electron-withdrawing group
- HRT: hydraulic retention time
- IBP: ibuprofen
- LOD: limit of detection
- LOQ: limit of quantification
- MBR: membrane bioreactor
- MBBR: moving bed biofilm reactor
- MBBR-MBR: moving bed biofilm reactor – membrane bioreactor

- MDL: method detection limit
- MLSS: mixed liquor suspended solids
- MLTSS: mixed liquor total suspended solids
- MLVSS: mixed liquor volatile suspended solids
- MQL: method quantification limit
- NTU: nephelometric turbidity unit
- OUR: oxygen uptake rate
- OUR_{end}: oxygen uptake rate in endougenous conditions
- PDR: physicochemical degradation rate
- R: recovery
- RO: reverse osmosis
- RSD: relative standard deviation
- SRT: solid retention time
- SS: suspended solids
- TOC: total organic carbon
- TSS: total suspended solids
- UV: ultraviolet
- VSS: volatile suspended solids
- WRRF: wastewater resource recovery facility
- WWTP: wastewater treatment plant

NOMENCLATURE

- $(1 - f_p)$: volatile biomass fraction
- μ_{m}: maximum growth rate
- μ_{emp}: empirical growth rate
- μ_{max}: maximum growth rate
- η: removal yield
- BDR: biological degradation rate
- b_{H}: endogenous respiration coefficient for heterotrophic biomass
- C: concentration
- C_0: initial concentration
- C_{BR}: concentration in the bioreactor
- C_{e}: concentration in equilibrium
- C_{eff}: concentration in the effluent
- C_{in}: concentration in the influent
- C_{pe}: concentration in the permeate
- C_{w}: concentration in the excess sludge
- e^-: electron
- f_{cv}: conversion factor
- Fe^{+2}: ferrous ion
- Fe^{+3}: ferric ion
- H^+: proton
- h^+: proton
- H_2O: water

- H_2O_2: hydrogen peroxide
- hv: energy
- k: physicochemical degradation rate
- k_{ap}: aparent constant
- k_{d}: total endogenous respiration coefficient
- K_{M}: semisaturation coefficient
- n: kinetic order
- OC: oxygen comsumpted
- OH^-: hydroxyl radical
- $OH^{\bullet}$: hydroxyl radical
- OUR_{end}: oxygen uptake rate in endogenous conditions
- OUR: oxygen uptake rate
- PDR: physicochemical degradation rate
- Q_{w}: excess sludge flowrate
- Q_{pe}: permeate flowrate
- Q_{eff}: effluent flowrate
- Q_{in}: influent flowrate
- R_{S}: oxygen consumption rate in dynamic test
- $r_{\mathrm{su,H}}$: substrate degradation rate of heterotrophic biomass
- r_{x}: growth rate
- S: substrate
- TiO_2: titanium dioxide
- V: volume
- X: total suspended solids

- X_{H}: heterotrophic biomass
- X_{T}: total suspended solids
- Y_{H}: yield coefficient
- Y_{H,O_2}: yield coefficient referred to oxygen
- $Y_{\mathrm{H,VSS}}$: yield coefficient for heterotrophic biomass