



Research article

Removal of ciprofloxacin from seawater by reverse osmosis

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ABSTRACT

Much of the deterioration of water resources is anthropogenically caused as a consequence of the incessant production of chemical compounds to obtain the quality of life that society demands today. This constant presence and harmful accumulation of these pollutants in different ecosystems have seen them emerge as a major concern both for human health and for environmental safety. Scientific advances have succeeded in legislating against, reducing and even eliminating priority pollutants, while new technologies are being constantly developed to identify and treat newly emerging pollutants. The objective of this work is the evaluation of the seawater reverse osmosis membrane as a method for the removal of an antibiotic present in seawater. The novelty of the study is that the tests were undertaken using water of high ionic strength. A critical selection of the antibiotic to be used in the study was carried out. The experiments were performed under constant pressure conditions, employing synthetic seawater in a pilot-scale unit with a commercial spiral-wound reverse osmosis membrane. Results are shown in terms of selectivity of the reverse osmosis process for antibiotic removal. The RO membrane element successfully reject most of the ciprofloxacin (removal rate >90%), with maximum rejection value of 99.96%.

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1. Introduction

Emerging pollutants (EPs) reach the environment from a variety of anthropogenic sources (Cámpo Gómez, 2003) and are distributed throughout all environmental matrices. Population growth and economic development (Barceló and López de Alda, 2008) contribute every day to the increased presence of these compounds. As a result of their high production levels (Bolong et al., 2008) and continuous emission into the environment, they have a negative impact on the environment irrespective of their degree of persistence (Petrovic et al., 2003). These types of pollutant are unregulated compounds (Noguera-Oviedo and Aga, 2016), characterized by appearing at mostly low concentrations (in the order of µg/l) (Noguera-Oviedo and Aga, 2016; Laprowth et al., 2012). They comprise a wide variety of chemical compounds, with the greatest concern centered on flame retardants, pesticide metabolites, drugs and their products of degradation through human waste and hormones (particularly estriol, 17-β-estradiol and 17-α-estradiol), pharmaceutical and personal care products and “life-style”

compounds (Barceló and López de Alda, 2008; Gil et al., 2012; Kimura et al., 2003).

The main route of intrusion into the environment of these pollutants comes from wastewater effluents that are discharged into the sea in most cases. For this reason, technological applications tend to focus on improving treatments of residual waters. As these treatments are designed to generally eliminate solids and fecal contamination, most do not specifically address the removal of EPs (Bolong et al., 2008; Petrovic et al., 2003; Andreozzi et al., 2003; Fischer et al., 2017). In fact, numerous scientific studies conducted in purified wastewater confirm EPs presence at trace levels (µg/L) or even higher (Sultana et al., 2017). On the other hand, the regeneration of purified wastewater allows completion of the entire water cycle, of particular importance in areas with scarce natural water resources, using different technologies including disinfection, reduction of salinity, etc.

Membrane-based processes have been gradually introduced in the regeneration process of purified wastewater in both secondary and tertiary treatments (Martinez et al., 2015), and are one of the main technologies which are also used in brackish water and seawater desalination. This widely implemented technology has proven to be a promising alternative (Bolong et al., 2008; Oller et al., 2011; Kimura et al., 2003), but there remains a need to evaluate it in terms of removal of these new micro-pollutants, which could

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double its effectiveness as a wastewater treatment process (WWTP).

In some cases, especially in coastal areas, the water intakes of seawater desalination treatment plants are located near the submarine outfalls of wastewater treatment plants. Consequently, if EPs are present in the discharge water they could potentially be reintroduced in the water cycle via the desalination plant water intake. As a result, research has tended to focus on the response evaluation of spiral wound reverse osmosis membranes as an EPs removal technology.

It should be noted that in Spanish legislation, and in particular Royal Decree 140/2003 of 7 February (BOE, 2003) which determines health criteria for the quality of drinking water, EPs substances are non-regulated. Many EPs compounds are new, and existing legislation may well need to be adapted if they are proven to affect human health.

1.1. Membrane technologies as pollutant treatment and removal method

Membrane technologies involve processes in which semi-permeable membranes acting as selective physical barriers are used to divide the feed stream into a permeate and a concentrate stream, thereby separating contaminants present in the wastewater (De la Macorra García and González, 2014). The main advantages of using these technologies include the removal of contaminants that are at low concentrations and/or dissolved in colloidal form. In addition, they allow continuous operation at moderate temperatures and with high selectivity control. These systems have a simple flow diagram, in addition to allowing modular and compact designs which do not require a lot of space, combine easily with other treatments and have no need for the use of additive products (Mulder, 1996; Rodríguez et al., 2006).

Among membrane technologies, reverse osmosis (RO), also known as hyper-filtration, is a membrane separation process which allows the removal of very small particles such as monovalent ions with diameters in the order of 10^{-3} – 10^{-4} μm . As mentioned above, there is a wide variety of emerging pollutants. Similarly, there are a large number of commercial RO membranes. Both membranes and contaminants have different physicochemical properties (Nghiem and Fujioka, 2016; Van der Bruggen and Vandecasteele, 2002). In the investigations of Dan Libotean et al. (2008), the relationship (both qualitative and quantitative) between the chemical structure of the pollutants and the RO membranes is demonstrated. Attending to the aforementioned work and the references cited therein, the rejection rate of EPs is governed by the physicochemical properties of the EPs (e.g. molecular size, charge, hydrophobicity, etc.) and the membrane element characteristics (e.g. configuration, pore size, permeability, etc.) and the operating conditions of the process (e.g. pressure, flux, ionic strength of the feed water, temperature, etc.). Therefore, the present study aims to investigate the evaluation of a spiral-wound reverse osmosis membrane on the removal rate of an antibiotic present in seawater. In order to study the possible interaction between de RO membrane element and the antibiotic a standard polyamide thin-film composite membrane element and a common antibiotic was selected.

1.2. Pharmaceutical products as pollutants

Although, at global scale, caffeine is one of the compounds most consumed by humans, studies such as those by Rosal et al. and Teijón et al. show that at national level (in Spain), the presence of pharmaceutical compounds in WWTP exceeds that of this psychoactive drug (1.589 $\mu\text{g/l}$), with recorded values of 5.714 $\mu\text{g/l}$ in the case of gemfibrozil and values higher than 2 $\mu\text{g/l}$ for the

antiepileptic carbamazepine (Rosal et al., 2010; Teijón et al., 2010; Matamoros and Salvadó, 2013). A European study that includes the analysis of 90 WWTP again confirmed higher values of pharmaceutical products compared to the 3 $\mu\text{g/l}$ maximum concentration of caffeine (Loos et al., 2013). In view of the above, it was decided to concentrate on the pharmaceutical sector for the development of the present research study.

The global pharmaceutical market currently represents revenues for pharmaceutical companies of over one trillion dollars, and continues to grow due to an ever-growing access to an increasingly comprehensive supply of pharmaceutical drugs, both in industrialized and developing countries (European Environment Agency, 2010; Arzneimittelhersteller, 2015).

From an environmental point of view, pharmaceuticals have distinctive characteristics compared to conventional chemical contaminants (Cortacans Torre et al., 2006). In fact, these products are made up of large and chemically complex molecules, with very diverse structure, molecular weight and shape. Generally, the molecules are polar and have more than one ionizable group. The pH of the solution in which the molecules are found will affect both their properties and the degree of ionization. This type of compound is quite persistent in the environment, with a permanence from more than one year to several years, as is the case of clofibrilic acid. Drugs appear in the environment both in their initial form and through their metabolites, which are more polar and water-soluble.

Pharmaceutical products are developed to be biologically active, and there is a strong possibility that both the pharmaceutical residues and their metabolites or degradation products may have a difficult-to-predict eco-toxicological impact on the environment (la Farré et al., 2008). One of the biggest concerns in recent years has been the presence of antibiotics in the environment because they may favor the development of resistant bacterial strains, which would render ineffective this type of medication (Noguera-Oviedo and Aga, 2016). An Australian study analyzed the resistance of two bacterial strains (*Escherichia coli* and *Xanthomonas maltophilia*) to six antibiotics detected in WWTP effluent (ciprofloxacin, tetracycline, ampicillin, trimethoprim, erythromycin and sulfamethoxazole) confirming that bacterial strains showed resistance to all six antibiotics (Costanzo et al., 2005).

1.2.1. Antibiotics

The term antibiotic can be defined as a substance obtained by chemical modification of natural compounds or through the synthesis of chemical compounds (Kümmerer, 2009) that inhibits or stops the growth of microorganisms such as bacteria, protozoa and fungi. The recognition of antibiotics as agents for the prevention and treatment of infectious diseases has ensured continuous growth of the market (Gothwal and Shashidhar, 2015), generating a total dependence and intensive use which have caused the parallel appearance of microorganisms resistant to them. This is reflected in the increased difficulty in treating some diseases (Davies and Davies, 2010), and results in a doubly negative impact affecting both people and the environment.

After an intensive bibliographic review of the long list of antibiotics, the type selected for this study belongs to the fluoroquinolone (FQs) class. This is due to their high rate of detection and influx in treated effluents worldwide. In China, a study undertaken by Dong et al. of 19 antibiotics reported that these compounds had one of the highest concentrations detected (5.411 $\mu\text{g/l}$) (Dong et al., 2016).

In another study in Australia, Watkinson et al. evaluated the presence of 28 antibiotics, where again this class, and more precisely ciprofloxacin fluoroquinolone, had one of the highest concentrations (4.6 $\mu\text{g/l}$) (Watkinson et al., 2007). In Spain, very high maximum concentrations of antibiotics have been recorded. Most

notably, ciprofloxacin was detected with a concentration value of 13.625 µg/l (Rosal et al., 2010) and in studies carried out in Gran Canaria island (Canary Archipelago, Spain) the same antibiotic had the highest recorded concentration level (20.310 µg/l) of all the antibiotics detected (Afonso Olivares et al., 2015; Fernández-Rodríguez et al., 2015). Consequently, for the purposes of the present study it was decided to focus attention on ciprofloxacin.

2. Experimental methods and materials

2.1. Ciprofloxacin

Ciprofloxacin is a broad-spectrum synthetic antibiotic belonging to the group of FQs. It is used to treat a wide variety of bacterial infections, such as infections of the respiratory tract, urinary tract, skin, bone, gastrointestinal tract, auditory canal, etc. The characteristic structure of FQs is the 4-oxo-1,4-dihydroquinoline ring as the central nucleus with a fluorine atom at the 6-position (see Fig. 1).

Its mechanism of action is to interfere in the replication of DNA by inhibiting the enzyme bacterial DNA gyrase and topoisomerase IV, both of which are fundamental for the replication, repair, transcription and storage of the DNA of the bacterium.

2.2. Spiral-wound RO membrane element for the pilot plant

In order to study the possible interactions between the EPs and

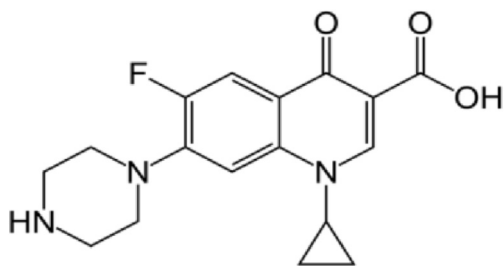


Fig. 1. Ciprofloxacin.

the membrane, a standard spiral-wound polyamide thin-film RO membrane RE2521-SHF (TORAY Industries) was used in the experiments, with a 99.7% salt rejection rate and a permeate flux of 1.14 m³/day under a concentration of 32,000 ppm NaCl. The effective surface area of the membrane is 1.1 m² (534 mm long and 64 mm in inner diameter).

2.3. Chemical reagents and equipment

2.3.1. Reagents

Commercial ciprofloxacin with ≥98% purity (Sigma-Aldrich) was selected as the antibiotic model, taking into account its neutral charge at pH 7, its presence in aquatic matrix and its molecular size.

The chemical agents used were: NaOH (Probus, 97.5%), NaHSO₃ (VWR, 50%), HCl (Labkem, 38%) and NaCl (Salins, 99.4%).

The feed water used in the RO tests was synthetic seawater prepared with commercial sea salt (sodium chloride as described above) and tap water at a fixed concentration of approximately 32 g/l (approximate value of salt concentration in seawater). Feed solution pH was adjusted to a value of 7 ± 0.2 by the addition of HCl and NaOH (as described above) and the silt density index (SDI) was less than 3. These values were determined in accordance with the recommendations of the membrane manufacturer and a prior bibliographic review. Sodium bisulfite was added to meet specifications for free chlorine tolerance (<0.1 ppm) (see Fig. 1).

2.3.2. Equipment

Experiments with this membrane were carried out in a modified version of the RO pilot plant scale model CE530 of the manufacturer Gunt Hamburg. A schematic diagram of the experimental set-up under constant pressure is shown in Fig. 3 (see Fig. 2).

The control and instrumentation elements consist of two manometers (PI) located in the feed flow and in the rejection flow, which together with the bypass and rejection valves (v-1, v-2) allow pressure control at the inlet and outlet of the membrane module and consequently control of the speed of the crossflow. The installation has three thermometers (TI) and three conductivity meters (QI), located in the feed, permeate and rejection flows, which allow control of the temperature and conductivity of the water in the process. Flow measurement is performed by two

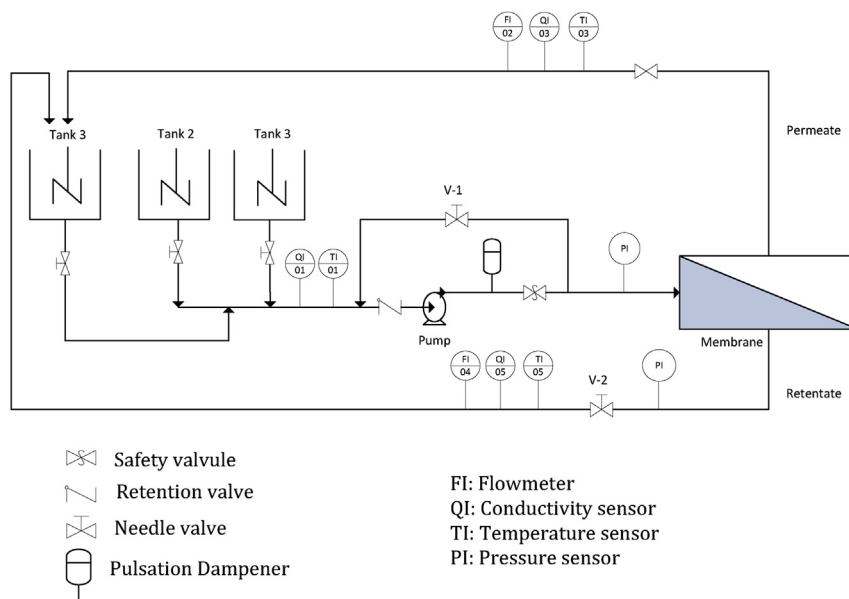


Fig. 2. Schematic diagram of the experimental set-up employed in the RO ciprofloxacin removal experiments.

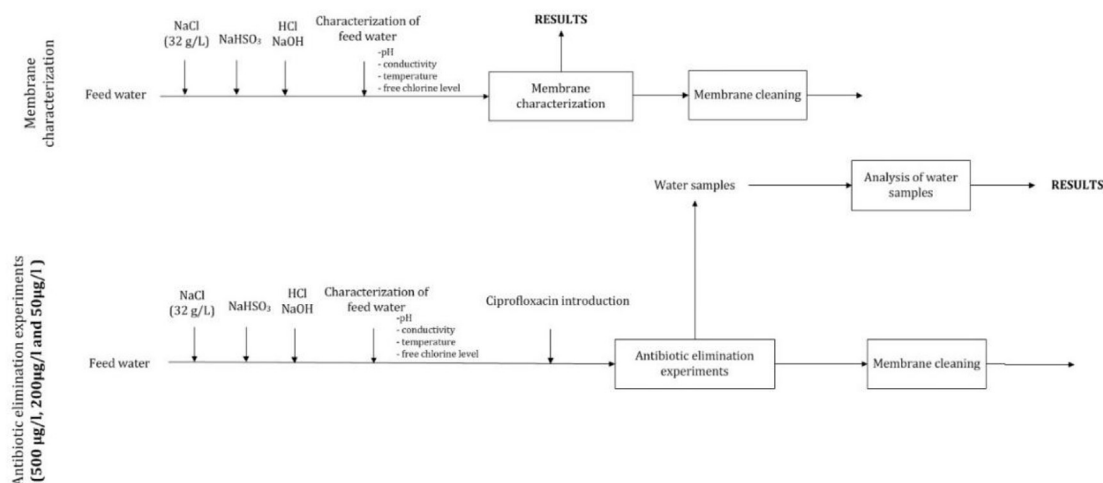


Fig. 3. Methodological sequence of the membrane characterization and ciprofloxacin tests.

Table 1
Ciprofloxacin properties.

Formula	C ₁₇ H ₁₈ N ₃ FO ₃
Molecular weight	331.347 g/mol
Density	1.5 g/cm ³
Melting point	255–257 °C
Pka	6.09
Log KOW	0.28
Charge (pH = 7)	0
Stokes radius	0.439 nm

turbine flowmeters (FI) located in the supply and rejection flows of the installation.

The 400 l feed solution is contained within three containers (100 l, 100 l and 200 l, respectively) until it is pressurized using a Kolben NP10/15–140 pump. The equipment is fitted with sampling valves.

2.3.3. Experimental set-up

2.3.3.1. Operating conditions. In order to determine the operating conditions of the tests, the following factors were taken into account:

- Specifications of the RE2521-SHF membrane manufacturer
- Simulation results obtained using the CSMPRO v5.0 software application
- Bibliographic review of membrane technologies

The limits of the operating conditions as recommended by the manufacturer to prevent rapid membrane deterioration with feed water with SDI <3 can be seen in Table 2.

The simulation of the process in the CSMPRO v5.0 software was

carried out by iteratively introducing data (characteristics and ionic analysis of the feed, process data, elements, stages, etc.), always seeking to respect the manufacturer's test conditions as specified on the membrane data sheet (Toray Chemical Korea Inc, 2521).

By means of the iterative process, the optimum conditions of permeate flow, reject flow rate and feed rate were calculated. Also shown in Table 2 are the operation data followed in the tests, which take into account the design specifications and the software simulation.

2.3.3.2. Membrane cleaning and characterization. Prior to the experiments, fresh water was filtered during 5 h through the virgin membrane to allow compaction and the removal of substances to preserve the membrane element. This process was carried out without increasing the pressure, so that there was practically no permeate flow, while most of the feed water was moving towards the reject stream.

Characterization tests were then performed to observe membrane behavior and performance against the rejection of salts, comparing it with the theoretical behavior obtained from software simulation. Due to the existence of two phases in the experimental procedure (as explained in the next section), two separate characterizations were performed, one for each experimental phase. Both characterizations were performed in the absence of the emerging pollutant, with a concentration of 32,000 ppm of NaCl and in the same operating conditions for each phase.

The characterization corresponding to the initial phase lasted approximately 2.5 h, using a total of 160 l of synthetic seawater with 80 l in each of the tanks of the plant. Characterization of the optimization phase of the tests had a duration of 3 h and was performed with 400 l of synthetic seawater. A third tank was incorporated into the system in order to use this volume, with the

Table 2
Design specifications (Toray Chemical Korea Inc, 2521) and operating conditions.

Design specifications		Operating conditions	
Parameter	Value	Parameter	Value
Maximum conversion (%)	19	Conversion (%)	8
Maximum operating pressure (bar)	82.7	Pressure (bar)	39.5
Maximum feed flow rate (m ³ /h)	1.3	Feed rate (m ³ /h)	0.25
Maximum permeate flow rate (m ³ /h)	2.7	Permeate flow rate (m ³ /h)	0.02
Minimum reject flow rate (m ³ /h)	0.23	Reject flow (m ³ /h)	0.23
Permeate flow (l/m ² h)	13–29	Permeate flow (l/m ² h)	18.18

according to ASTM D 4516-00 ([ASTM D 4516-00](#)).

3.2. Experimental protocol phases

The experimental protocol was divided into two phases: (1) antibiotic removal under variable temperature (22–30 °C), and (2) antibiotic removal under constant temperature (25 °C).

Because laboratory-scale recirculation processes produce an increase in temperature, and thus an increase in permeate flux and salt passage, the second phase arises from the need to improve the procedure to obtain more representative operating conditions.

In both phase studies, the same number of experiments were performed, with identical concentrations of ciprofloxacin.

During the initial phase, the total volume of feed water used in the experiments was 160 l, using two tanks of 80 l each. These tanks were connected in parallel and received the permeate and rejection flows of the system.

During the second phase and in order to maintain constant temperature in the EPs removal tests, the total volume of feed water was increased to 400 l with the incorporation of a new 200 l feed tank.

3.3. Sample analysis

The samples were collected in dark glass bottles (avoiding UV degradation), adjusted to $\text{pH } 3 \pm 0.2$ and stored at 4°C in order to maintain sample integrity by inhibiting microorganism growth. Filtration pretreatment with $0.65\text{ }\mu\text{m}$ membrane filters (Millipore) was subsequently performed in order to minimize interferences and possible obstructions during the extraction phase.

Samples were then subjected to solid phase extraction (SPE) by retaining the analyte at a concentration 40 times greater than the initial one. Oasis HLB polymer cartridges were used in this stage. In addition, the interferences were cleaned with a consequent elution of the analyte by passing it through a selective solvent (methanol CH₃OH).

High-performance liquid chromatography (ProStar410, Varian) coupled to a fluorescence detector (HPLC-FD) allowed detection and quantification of the antibiotic (see Fig. 4).

This method was developed and validated in the laboratory of the environmental chemical analysis group of the University of Las Palmas de Gran Canaria (Spain) (Montesdeoca-Esponda et al., 2012). The limit of quantification (LOQ) of the applied method (SPE-HPLC-FD) is 0.24 ng/ml and the limit of detection (LOD) 0.072 ng/ml, with a relative standard deviation (RSD) of 7.44%

Normalization of the experimental data was performed

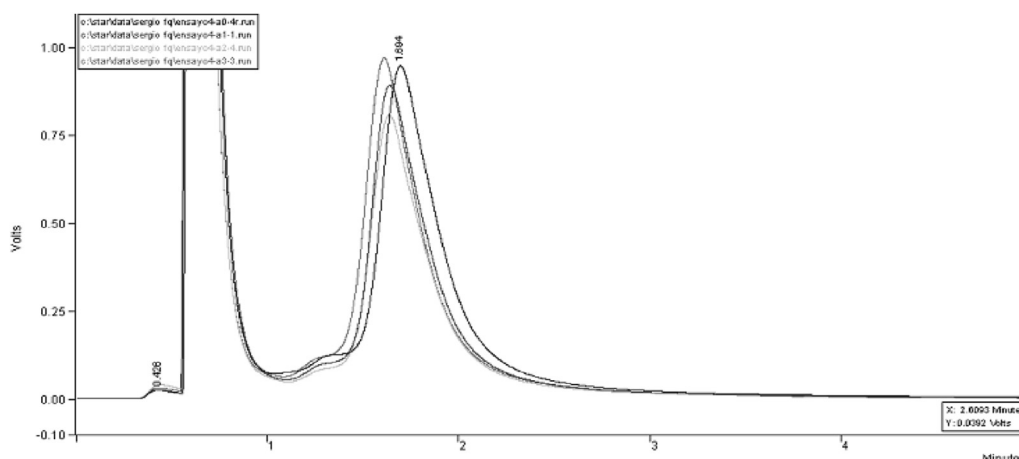


Fig. 4. HPLC-FD chromatogram of ciprofloxacin in feed water at different sampling times.

(Montesdeoca-Esponda et al., 2012).

4. Results and discussion

All experiments were carried out under constant pressure, flow rate and permeate flow.

Fig. 5 shows permeate flux during membrane characterization in the two phases, under variable and constant temperature conditions, respectively. Fig. 6 shows temperature evolution during characterization in the initial phase.

It can be seen that permeate flux under constant temperature is more stable. Even when permeate flux was normalized under the same operation conditions, the permeate flux in the first phase still showed clear instability.

The visible decrease in permeate flux in the second phase (13.6 l/m²h) compared to the characterization of the initial phase (16.1 l/m²h) may be due to the temperature effect and membrane compaction itself.

In terms of salt rejection, the same progress toward stability is observed with the change from the initial to the optimization phase. The instability of the initial phase permeate flow causes a rejection of salts with an average value of 98.3%, which is below the 98.5% rejection obtained in the second phase (see Fig. 7).

The experiments were performed at different ciprofloxacin concentrations of 50, 200 and 500 µg/l. The total duration of each test was 3 h, while the operating conditions were the same as those used in the membrane characterization test.

The experimental results, plotted against the percentage (%) of antibiotic rejection, are shown in Figs. 8 and 9. Table 3 summarizes

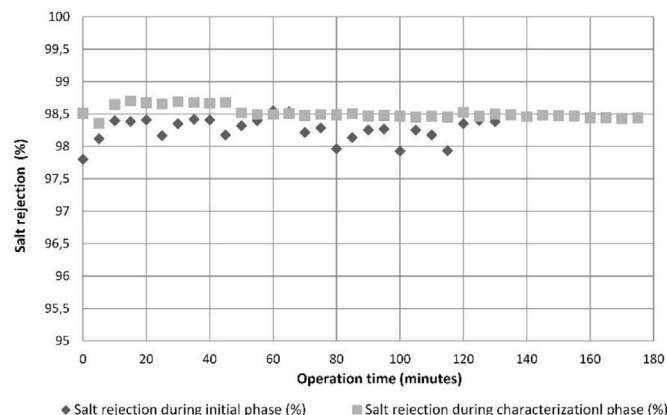


Fig. 7. Salt rejection evolution during characterization in the initial phase vs during characterization in the optimization phase.

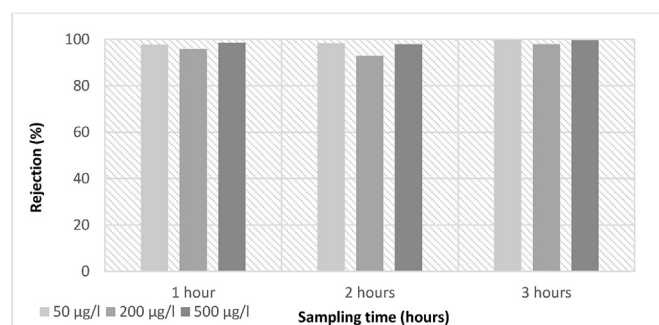


Fig. 8. Rejection obtained during the initial phase.

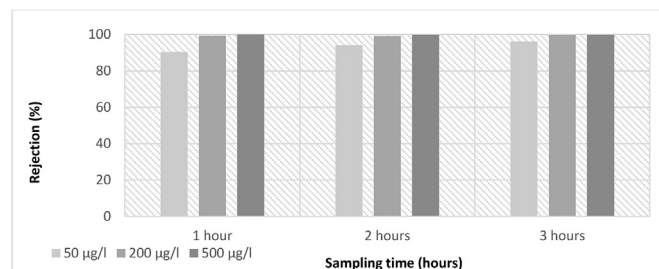


Fig. 9. Rejection obtained during the optimization phase.

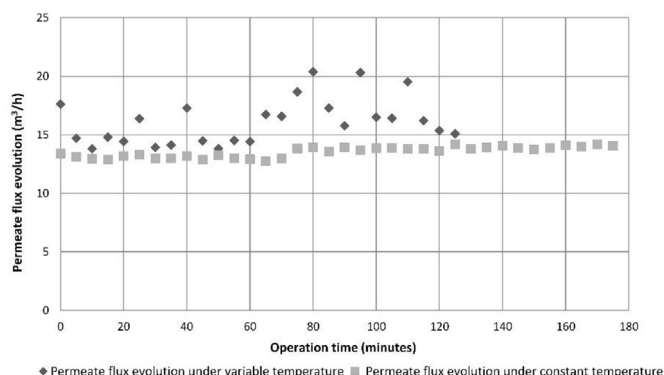


Fig. 5. Permeate flux evolution during initial membrane characterization under variable temperature vs during membrane characterization under constant temperature.

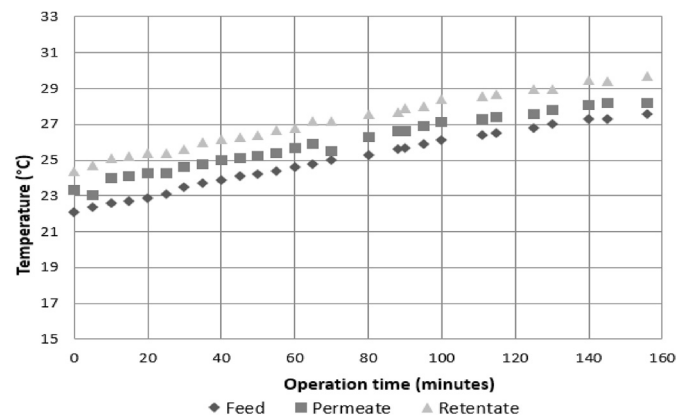


Fig. 6. Temperature evolution during characterization in the initial phase.

the variable temperature and salt rejection values in the phase 1 tests.

The results of antibiotic rejection obtained during the tests, both in phase 1 and 2, do not show significant variations over the duration of each test, with very similar rejection values being obtained in the three samples taken (Figs. 8 and 9). Therefore, in spite of the increase in temperature, no repercussions were observed in the rejection values obtained during the tests.

Throughout the ciprofloxacin removal tests performed during this investigation, rejection values of above 90% were obtained, with values in some cases higher than 99%. In some published studies on the removal of pharmaceutical products using RO, rejection values of 97.2–100% have been obtained for antibiotics of the FQs group (Dolar et al., 2009; Košutić et al., 2007). A study of EP removal by nanofiltration (NF) achieved rejection values for ciprofloxacin slightly higher than 85%, while for ofloxacin and norfloxacin (FQs antibiotics), rejection values of 85–90% were

Table 3

Temperate and rejection values during the initial phase tests.

Time	1 h		2 h		3 h	
	Concentration (µg/l)	T (°C) Rejection (%)	T (°C) Rejection (%)	T (°C) Rejection (%)	T (°C) Rejection (%)	T (°C) Rejection (%)
50	26	98.7	28	95.8	30	97.8
200	27	97.9	28	92.9	30	98.3
500	26	99.6	28	97.9	29	99.7

obtained (Wang et al., 2015). Another study using membrane biological reactors to remove emerging pollutants obtained 94% rejection rates for ofloxacin (Radjenovic et al., 2007). These published values show that the results obtained in the study undertaken in the present paper are comparable to those found in the literature. In terms of rejection, the RO results are superior to those found in other membrane processes. In addition, most of the above mentioned studies were performed in a laboratory unit which employs flat sheet membrane pieces, which is not representative of real scale seawater industrial applications.

In both phases, better rejection results were obtained in the 500 µg/l ciprofloxacin concentration tests, while the lowest values were obtained during the first test (50 µg/l ciprofloxacin concentration) of the second phase. The increase in the concentration of ciprofloxacin in the feed water should cause a decrease in the rejection capacity, attributed to the effect of concentration polarization (higher concentration gradient between the membrane sides). However, the increase in the concentration of ciprofloxacin does not appear to cause a greater net transport of sales through the membrane. In these cases, results in term of salt rejection differ only by about 2%. This highlight that this differences can attribute to the sensitive of the equipment used for the analysis, where relative standard deviation (RSD) at higher concentration are lower (see Table 4).

Based on the results, the following hypotheses can be made for the possible ciprofloxacin acting rejection mechanisms by reverse osmosis:

- The high rejection efficiency can be not explained taking into account possible electrostatic repulsion between the ciprofloxacin and the membrane element as the ciprofloxacin its uncharged at neutral pH and the polyamide thin-film composite membrane used in the experiments contains ionizable functional groups with a negative charge.
- X. Wang et al. investigated the rejection ratios of 40 trace organic compounds by nanofiltration (NF) membrane. The primary retention mechanism responsible for its removal were the steric hindrance effect. However, the steric (size) of ciprofloxacin molecules (see Table 1) is similar than the average pore size of the RO membrane element (<0.001 nm). This shows a possible convective transport of the ciprofloxacin trough the pores of the membrane. Therefore, the retention of the ciprofloxacin through

the membrane could be explained to the short-term by the sieving mechanism.

- The possible retention mechanism that govern ciprofloxacin removal it is related with the psychochemical properties of that antibiotic, mainly hydrophobicity adsorption and hydrolysis. The ciprofloxacin due to its neutral charge presents a moderate hydrophobicity (LogP = 1.625 (Wang et al., 2015)) and thus it could be partly adsorbing to the membrane.

According to Wang et al. (2015), the hydrolysis played an important role in the retention of the ciprofloxacin by NF membranes as it was one of the most rapidly antibiotic hydrolyzed in low ionic strength of the feed water (10 mmol/l NaCl). However recent investigations related to ciprofloxacin by-products in seawater environment highlight that FQs are resistant to hydrolysis due to chemical stability of the quinolone ring (Ziarrusta et al., 2018).

All these findings suggest that both the sieving mechanism and the hydrophobicity adsorption occurs simultaneously and their relative contributions need a further study.

To conclude the results section, the error rate in the antibiotic analytical detection method that was used is shown in Table 4. This table lists the average range obtained through the elaboration of a material balance of each test based on the concentrations detected by the HPLC and the flow rates of the pilot plant. In this analysis, the values were examined as absolute values, confirming that test performance was satisfactory, since the values obtained were within the 20% percentage of error stipulated by the solid phase extraction analytical method (Afonso-Olivares et al., 2013).

The error increase greater than 20% in both analyzes of 50 µg/l can be attributed to the difficulty of manipulating such small concentrations in both the analytical and experimental phase.

While this work presents specific rejection results, the authors are aware that in the future it will be necessary to expand the number of tests in order to be able to carry out an adequate statistical treatment.

The objective of the present study is the analysis or evaluation of RO membranes from the point of view of their performance in the elimination of ciprofloxacin as a food safety measure (in the event that this type of contaminant should reach an RO desalination plant). Further studies are nevertheless required to determine pollutant degradation rates in the brine. In recent years, some studies have been carried out on ciprofloxacin degradation in aquatic matrices. The methods used in these studies include, most notably, advanced oxidation processes (AOP), which are presently the most commonly studied methods for the degradation of all manner of antibiotics (Homem and Santos, 2011). The AOPs can be essentially defined as processes that involve the generation of OH⁻, hydroxyl radicals, and can be differentiated by the method used to obtain them. Thus, hydroxyl radicals can be obtained from ozone (O₃), hydrogen peroxide (H₂O₂), by using catalysts or with UV light (Homem and Santos, 2011; Glaze et al., 1987).

Though no specific studies of ciprofloxacin degradation in seawater have been found by the authors of the present paper, some research has been conducted into potential ciprofloxacin degradation methods. For example, a study of photo-Fenton mineralization of ciprofloxacin, using a modified iron nano-composite based on laponite clay (Fe-Lap-RD) as a heterogeneous catalyst, in the presence of hydrogen peroxide and UV light, achieved complete degradation of the antibiotic after 30 min of reaction (Bobu et al., 2008). An evaluation was also made of the Fenton oxidation process, in this case with Fe²⁺ as a catalyst and in the presence of H₂O₂, giving maximum percentages of antibiotic degradation higher than 70% (Giri and Golder, 2014). In a study of ciprofloxacin degradation by ozonolysis in the presence of

Table 4

Antibiotic error rate obtained from material balance analysis.

Antibiotic concentration (µg/l)	Average percentage error (%)
<i>Initial phase. Variable temperature</i>	
50	27.06
200	13.05
500	18.63
<i>Optimization phase. Constant temperature</i>	
50	24.73
200	11.85
500	10.76

hydrogen peroxide in a bubble reactor, maximum degradation values of 95% were reached at 60–75 min of reaction (De Witte et al., 2009). Another study achieved a photocatalytic degradation rate of ciprofloxacin higher than 97% at 30 min of reaction, using UV light and TiO_2 as catalyst (An et al., 2010).

5. Conclusions

Reverse osmosis is one of the processes widely used for brackish and seawater desalination, so its use is extended even to obtain drinking water and other non-potable uses (water reuse).

The main objective of the present study is the analysis or evaluation of RO membranes from the point of view of their performance in the elimination of ciprofloxacin as a food safety measure (in the event that this type of contaminant should reach an RO seawater desalination plant).

A laboratory-scale methodological sequence was generated consisting of membrane characterization and evaluation of the reverse osmosis process for the removal of ciprofloxacin, an emerging pollutant.

It was determined that a spiral-wound seawater reverse osmosis membrane rejects ciprofloxacin under the operating conditions and doses of the emerging pollutant used in the performance tests.

Ciprofloxacin removal rates were higher than 90% in all the tests, with maximum rejection values of 99.96%. The percentages of rejection were higher than previously published values for the removal of fluoroquinolones using nanofiltration processes and biological membrane reactors.

Despite an increase in temperature during the experiments in phase 1, the rejection of the antibiotic obtained by the seawater reverse osmosis process did not appear to be affected.

There was no significant variation in the percentages of rejection obtained between the different sampling hours performed for each test of a single sample.

Though it was not possible to subject the results to a statistical analysis due to the low number of samples, they do allow a precise quantification of membrane performance.

Though no specific studies of ciprofloxacin degradation in seawater have been found by the authors of the present paper, some research has been conducted into potential ciprofloxacin degradation methods. In order to establish an adequate post-treatment of the rejection obtained, studies on the degradation of ciprofloxacin in seawater are needed.

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