

Removal of a mixture of pharmaceuticals sulfamethoxazole and diclofenac from water streams by a polyamide nanofiltration membrane

Daniela Gomes, Mafalda Cardoso, Rui C. Martins, Rosa M. Quinta-Ferreira and Lícínio M. Gando-Ferreira

ABSTRACT

Wastewater treatment plants are not specially designed to remove pharmaceutically active compounds (PhACs), since these substances are toxic and bio-refractory. This paper aims to investigate and optimize the performance of the Trisep TS80 nanofiltration (NF) membrane for the removal of a mixture of two of the most detected PhACs in municipal wastewaters worldwide, sulfamethoxazole and diclofenac. Several NF tests were carried out to study the rejections of these contaminants both spiked in demineralized water, filtrated water taken from Mondego River and secondary effluent coming from a municipal wastewater treatment plant. Among the several studied operating variables, pH was the one that most affected the contaminant rejection and membrane permeability. In the case of synthetic effluent, an applied pressure of 10 bar and pH 7 were determined as the best operating conditions, which allowed almost total chemical oxygen demand retention and a global contaminant rejection of 96.3% to be achieved. The application of different water matrices (river water and secondary municipal effluent) had no relevant impact on process efficiency. *Vibrio fischeri* luminescence inhibition tests revealed that treatment by nanofiltration reduced acute toxicity of all studied effluents.

Key words | diclofenac, emerging contaminants, fouling, nanofiltration, sulfamethoxazole

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INTRODUCTION

Surface and groundwater are the main resources for sustainable drinking water production throughout the world. However, large amounts of this water are contaminated by refractory organic substances derived from industrial, domestic and farming activities (Radjenović *et al.* 2008; Vergili 2013). Special focus is being given to pharmaceutically active compounds (PhACs) which are reaching water due to their increasing usage every year (Esplugas *et al.* 2007; Aguinaco *et al.* 2012). The conventional biological treatment processes do not tend to remove such compounds (Ternes 1998; Johnson & Sumpter 2001; Esplugas *et al.* 2007).

Two of the PhACs most frequently detected in raw sewage and secondary treated effluent throughout the world are sulfamethoxazole (SMX) and diclofenac (DCF) (Beltrán *et al.* 2009) and, therefore, they were selected for this study. SMX is an important member of the sulfonamide antibacterial group and is probably one of the most widely

prescribed antibiotics for animal and human use (Nghiem *et al.* 2006; Wu *et al.* 2010; Simon *et al.* 2011). DCF is a common anti-inflammatory drug used as analgesic to reduce inflammation and for the relief of pain and requires environmental monitoring in the EU member states (Vieno & Sillanpää 2014).

The presence of PhACs in the environment can affect the water quality and potentially impact drinking water supplies, ecosystems and human health (Heberer 2002). Thus, it is necessary to treat adequately effluents containing pharmaceuticals before discharging them.

In the past few years, pressure-driven separation membrane technologies like nanofiltration (NF) or reverse osmosis (RO) have been the focus of many studies, as an alternative to conventional treatment processes since they are energetically efficient and environment-friendly. Moreover, several works based on the use of these technologies

have proven that they are efficient for the removal of a wide variety of organic contaminants from water such as pesticides (Berg *et al.* 1997; Hofman *et al.* 1997), dyes (Marcucci *et al.* 2002) and PhACs (Verliefde *et al.* 2008; Simon *et al.* 2009).

NF is usually applied to separate organic solutes of low molecular weight (between 200 and 1,000 Daltons) and inorganic salts with sizes ranging between 1 and 8 μm . It offers higher permeate fluxes with lower operating pressure than RO and better retention than ultrafiltration for small molecules such as sugars, amino acids, peptides and ions (Luo & Wan 2013).

The dominant rejection mechanism of NF is dependent on the feed effluent pH since both membrane surface charge and degree of deprotonation of compounds vary according to pH (dissociation of the functional groups of the molecules as a function of pKa) (Simon *et al.* 2011). Retention of neutral solutes is mostly due to size exclusion or steric hindrance effects between the solutes and membrane matrix. In this case, solutes with a size larger than the pore size of the membranes are efficiently separated (Verliefde *et al.* 2008). However, Van Der Bruggen *et al.* (1999) verified that the retention of organic compounds by size exclusion is also affected by their dipole moment. Moreover, hydrophobic interactions between solutes and membrane polymeric matrix (i.e. hydrophobic solutes can adsorb onto hydrophobic membrane surface) promote solute diffusion through the membrane pores, resulting in a decrease of the rejection of hydrophobic solutes (log value of octanol/water partition coefficient $\log K_{ow} > 2$) (Kimura *et al.* 2003; Braeken *et al.* 2005).

Most NF membranes are negatively charged (negative zeta potential) at neutral and alkaline pH due to acid functional group dissociation on their surface. Thus, the rejection of organic microcontaminants is mainly attributed to electrostatic interactions between charged solutes and the charged membrane surface (Ozaki & Li 2002).

Also, the amount and nature of natural organic matter (NOM) (Nghiem & Hawkes 2007) in the water matrix are factors that can affect contaminant retention.

Many studies investigating SMX and DCF retention by NF membranes have been published; however, these researches were carried out mainly with individual contaminants spiked in demineralized water. This technology has not yet been studied and optimized to treat efficiently complex matrixes (containing several contaminants). Thus, the main goal of the present paper is to study the effect of several operative variables (pH, drop pressure and ratio between contaminants' concentration) on the removal of a mixture

of SMX and DCF from aqueous solutions by NF. Moreover, it aims to evaluate the impact of the water matrix on contaminant rejection and on the inhibitory effect caused by the toxicity of the raw effluent and the treated samples. This work also aims to analyze the membrane's fouling.

MATERIAL AND METHODS

Nanofiltration membrane

The commercial flat-sheet membrane TS80 manufactured by Trisep Corp. and purchased from Sterlitech Corp. was used. This membrane has a filtration area of 140 cm^2 and consists of a thin film composite with a cross-linked aromatic polyamide top layer. According to the data provided by the manufacturer, the molecular weight cut-off (MWCO) of the TS80 lies between 100 and 200 Da and operation pH should be between 2 and 11 to avoid its damage. Verliefde *et al.* (2008) measured the membrane zeta potential as a function of pH and verified that the TS80 has decreasing (and negative) zeta potential with increasing pH. The TS80 membrane was selected for this research considering previous works in which it or membranes with similar properties presented high rejection values for the studied contaminants (Verliefde *et al.* 2008; Wu *et al.* 2010). However, the removal of SMX and DCF mixtures was not examined in any of these researches.

Model solutions preparation

Sulfamethoxazole and diclofenac sodium salt of high purity grade (>98%) were obtained from Alfa Aesar and stored at 5 °C. The most relevant physicochemical properties of each one are provided by Vergili (2013), Simon *et al.* (2011) and Wu *et al.* (2010). Solutions of both PhACs were prepared using demineralized water, filtrated river water and municipal secondary effluent coming from a biological treatment process (trickling filter beds).

Nanofiltration set-up and experiments

Nanofiltration experiments were carried out in a cross-flow operation mode using a flat-sheet laboratory-scale membrane filtration unit (SEPA CF II, Osmonics). The feed stream was pumped to the membrane module by a diaphragm pump. The pressure drop (ΔP) was regulated using a concentrate flow control valve and measured with a precision manometer (SPAN) and the concentrate flow rate was monitored by a

flowmeter. The membrane filtration system was operated in recycle mode, since both permeate and concentrate returned to the feed reservoir (Gomes *et al.* 2010).

Water flux was measured for various pressure differences (3–18 bar) to evaluate the membrane permeability. To determine membrane average pore size, a feed solution containing 127 mg L⁻¹ (as total organic carbon – TOC) of xylose (>99%, Fluka) was used. In the case of mass transfer coefficient measurement, experiments were firstly performed to measure water flux. Then, flux and salt concentration in the permeate stream were measured at 10 and 18 bar after adding 0.1 M NaCl solution to the feed reservoir.

In experiments with pharmaceuticals, pH varied from 3 to 8, whereas applied pressure varied from 5 to 18 bar, taking into account the characteristics of the membrane and that SMX and DCF concentration in the feed solution varied from 0 to 60 mg L⁻¹, considering the goals of the trials and the analytical techniques' detection limit.

After each trial, the membrane was washed and the water flux was measured to calculate the membrane permeability and, hence, the fouling index (FI). To evaluate the cleaning step impact on the membrane permeability, two cleaning approaches were carried out using demineralized water or an acid solution. The acid cleaning consisted of three steps: demineralized water followed by HCl aqueous solution (0.5 mM; pH 3.3) and again demineralized water. Each one of these steps lasted about 10 minutes (wash volume of 5 L) and was performed at 10 bar.

Preliminary experiments carried out by Gomes *et al.* (2010) showed that the system needs around 15 minutes to reach steady-state conditions. In all experiments, the concentrate flow rate was 0.58 L min⁻¹, temperature was maintained between 16 and 20 °C and feed pH was adjusted by addition of 2 M HCl (37%, Sigma-Aldrich) or 2 M NaOH (98%, Panreac) solutions.

Analytical methods

The target compounds (SMX and DCF) were detected and quantified by high performance liquid chromatography (HPLC) analyses, in which 20 µL of sample were injected through an autosampler (SIL-20AC HT, Shimadzu). Acetonitrile (HPLC grade, Carlo-Erba) and ultrapure water (acidified at pH 3 by addition of orthophosphoric acid (Fluka) 25%) at a 40:60 volume ratio and with a flowrate of 1 mL min⁻¹ were used as mobile phase. The stationary phase was a C18 column (SiliaChrom) at 50 °C and detection was performed at 270 nm for SMX (Dantas *et al.*

2008) and at 277 nm for DCF (Beltrán *et al.* 2009) in a UV detector (SPD-M20A, Shimadzu).

Chemical oxygen demand (COD) was determined by potassium dichromate closed reflux method described by ISO 6060 (ISO 1989). The used thermoreactor was the ECO 25, VELP Scientifica, and the absorbance at 445 nm was measured using a photometer (Photolab S6, WTW).

Bioluminescence tests were used to determine the toxicity of the raw wastewaters and treated samples to assess their impact in ecosystems. LUMISTox tests (Dr. Lange, Germany) were performed according to the standard method DIN/EN/ISO 11348-2 (ISO 2007), which is based on the light inhibition of luminescent marine bacterium *Vibrio fischeri* (LCK 480 kit) caused by the toxic effect of the contaminants when incubated at 15 °C in LUMIStherm (Dr. Lange, Germany). The samples can be considered as toxic when the light inhibition is higher than 30% (Miralles-Cuevas *et al.* 2017).

Atomic force microscopy (AFM) was performed to compare surface topography of the virgin and used membrane. The membrane is made of polyamide, which is a soft material; the method used was semicontact with a NSG10 tip and a radiant frequency of 285 kHz. The samples were placed in a sapphire holder and the equipment placed over an anti-vibrational table (Accurion). A 5 µm × 5 µm surface topography was done for both virgin and used membrane and their roughness evaluated using the AFM software.

The total dissolved solids (TDS) in the natural water matrixes were determined according to standard methods (Greenberg *et al.* 1992). The amount of inorganic ions Ca²⁺ and Mg²⁺ dissolved in river water and secondary effluent was measured by atomic absorption spectroscopy (Perkin-Elmer 3300). A TOC analyzer (Shimadzu TOC-5000A) was used to indirectly quantify the xylose in the feed and permeate samples. The concentrations of NaCl were indirectly determined by conductivity measurements (Hanna Instruments 2550) and pH was measured using Crison micro pH 2002 equipment.

RESULTS AND DISCUSSION

Wastewaters and their physicochemical properties

The influence of feed water chemistry on retention of the selected PhACs was studied by using three feed water types. The first water type used was synthetic effluent, in which the contaminants were spiked in demineralized

water to evaluate the effect of several operating conditions on the nanofiltration efficiency. In turn, to assess the effect of the presence of NOM and mono- and divalent ions on the retention of the target contaminants, experiments were performed using solutions prepared with filtrated water coming from Mondego River and municipal secondary effluent collected from a biological treatment process (trickling filter beds). The most important physicochemical properties of each one are presented in Table 1.

Regarding pH, synthetic water presents an acid character (pH 5.67) while the river water and secondary effluent are neutral (pH 6.87 and 6.67). The COD of both wastewaters is very similar; however, as expected, the river water and secondary effluent have a slightly higher COD due to the presence of NOM. Despite the COD of the feed waters being lower than the legal limit for their discharge into the water resources according to Portuguese Decree Law N° 236/98 of 1st August (150 mg L⁻¹), the main concern related to these effluents is their high toxicity and, consequently, their negative impact over life forms when released into the environment without any treatment. The *Vibrio fischeri* light inhibition percentage after 30 minutes of exposition to the contaminants is similar for all used matrixes (~70–75%), which means that the effluent's toxicity is mainly due to the PhACs. Moreover, Table 1 shows that the real matrixes present divalent ions (Ca²⁺ and Mg²⁺) and dissolved solids, which are higher for the secondary effluent.

Membrane characterization

The membrane permeability was determined, experimentally, by measuring pure water flux as a function of applied pressure.

Plotting the experimental results, the membrane permeability is the slope of the straight line obtained by fitting Darcy's law through least squares method. The results obtained for three runs shown in Figure 1 allowed us to determine the membrane permeability as $1.864 \times 10^{-6} \text{ m s}^{-1} \text{ bar}^{-1}$, which is similar with that found by Verliefde et al. (2008). Moreover, considering the water viscosity at 16 °C equal to $1.10 \times 10^{-8} \text{ bar}^2 \text{ s}$ (Kestin et al. 1978), a membrane resistance value equal to $4.87 \times 1,013 \text{ m}^{-1}$ was found.

Simultaneous rejection of SMX and DCF by nanofiltration

Effect of initial pH

Single-pharmaceutical solutions. To better understand the effect of pH on NF performance to treat a mixture of SMX and DCF, first, experiments were performed with the individual contaminants (60 mg L⁻¹) in demineralized water. Figure 2 shows the effect of feed water pH on SMX rejection measured through HPLC analysis (Figure 2(a)) and COD (Figure 2(b)). The retention of SMX or DCF solutions by nanofiltration can be explained by the mechanisms of size exclusion and hydrophobic and electrostatic interactions, depending on the initial pH.

At low pH, the Trisep TS80 membrane is practically uncharged (Verliefde et al. 2008) and SMX molecules regain their protons and become neutral. Then, no electrostatic repulsion exists, and rejection of the solutes is only governed by size exclusion or hydrophobic interactions between solute molecules and membrane surface. However, results reported by Verliefde et al. (2008) show that the size exclusion is not always the mechanism that determines

Table 1 | Characterization of the effluents used in the experiments

| | Synthetic effluent | River water | Secondary effluent |
|--|--------------------|--------------|--------------------|
| SMX concentration (mg L ⁻¹) | 30 | 30 | 30 |
| DCF concentration (mg L ⁻¹) | 30 | 30 | 30 |
| pH | 5.67 ± 0.24 | 6.87 ± 0.02 | 6.67 ± 0.02 |
| COD (mgO ₂ L ⁻¹) | 84.25 ± 6.01 | 87.45 ± 1.46 | 87.15 ± 0.21 |
| <i>V. fischeri</i> light inhibition ^a (%) | 70.47 ± 0.13 | 74.55 ± 0.87 | 72.86 ± 0.96 |
| TDS (mg L ⁻¹) | – | 98 ± 8.49 | 514 ± 31.11 |
| Ca ²⁺ (mg L ⁻¹) | – | 3.39 | 27.58 |
| Mg ²⁺ (mg L ⁻¹) | – | 3.40 | 23.40 |

Mean ± standard deviation.

^aAfter 30 minutes of exposure.

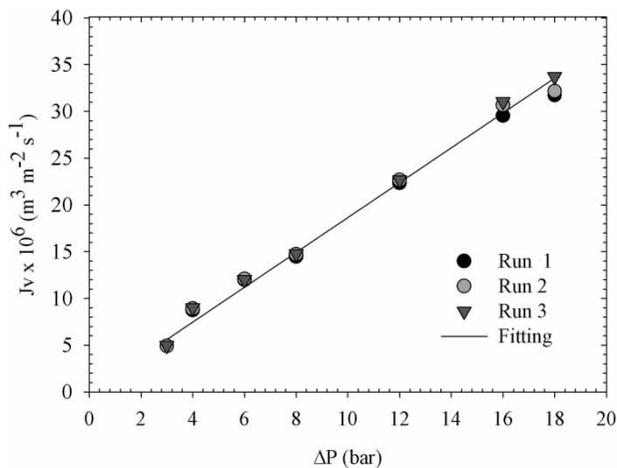


Figure 1 | Variation of permeate flux (J_v) with pressure for pure water.

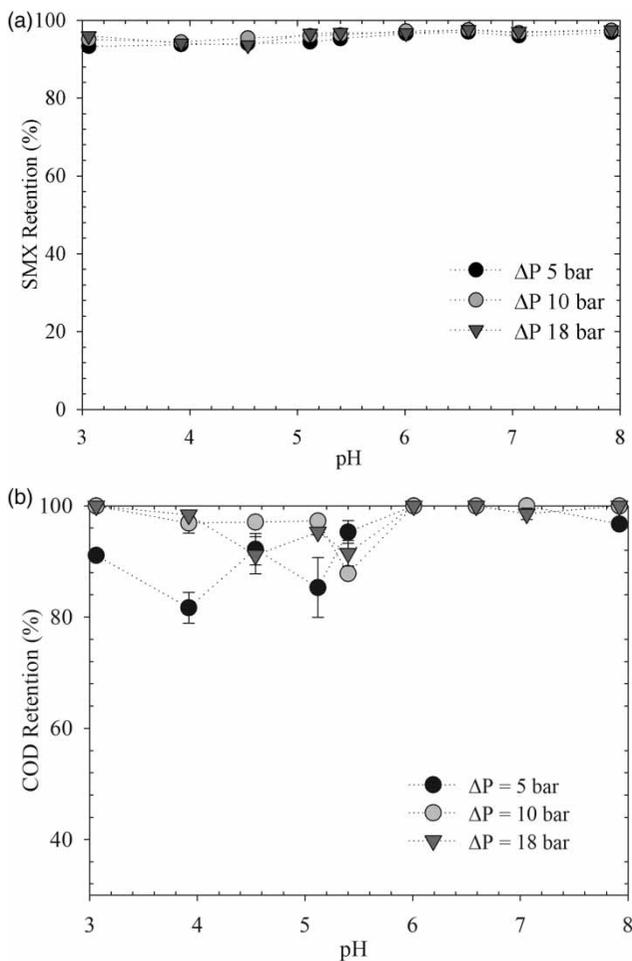


Figure 2 | Effect of the feed water pH on (a) SMX and (b) COD retention at different applied pressure values (5, 10 and 18 bar).

rejection, and electrostatic effects, especially hydrophobic interactions, play an important role in acidic pharmaceutical

retention, such as SMX. So, since the membrane is hydrophobic and SMX is hydrophilic, hydrophobic interactions may explain its high retention (93.2–97.2%).

When the feed pH increases, the charge density on the membrane surface tends to increase due to carboxylic groups dissociation. Thus, at pH values above 6 ($\text{pH} > \text{pK}_{a2}$), both the membrane surface and SMX molecules are negatively charged, and then the dominant mechanism is electrostatic repulsion between them, which leads to high rejections (96.0–97.5%).

Regarding DCF, Figure 3 shows the effect of water feed pH on its retention calculated based on HPLC analysis (Figure 3(a)) and COD (Figure 3(b)) measurements. As can be seen from Figure 3(a), the DCF retention is high (about 100%) and the process efficiency is very little affected by pH. A similar behavior was observed by Verliefe *et al.* (2008), who obtained high DCF rejections (about 97%) in the range of pH studied (3–10), using the TS80 membrane.

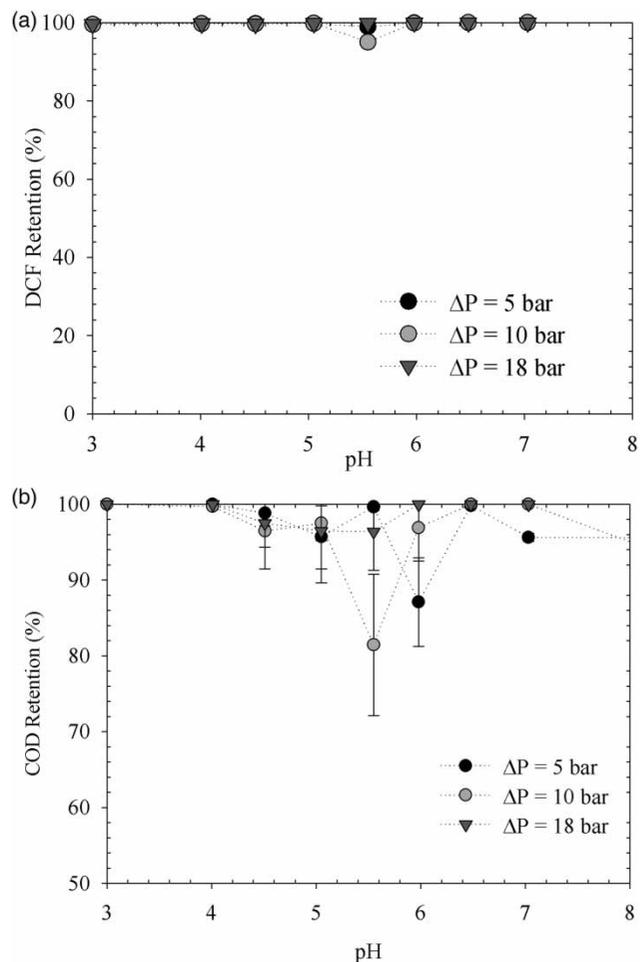


Figure 3 | Effect of the feed water pH on (a) DCF and (b) COD retention at different applied pressure values (5, 10 and 18 bar).

At lower pH, acid pharmaceuticals regain their protons and become neutral, and a decrease in rejection with increasing hydrophobicity is observed (Verliefde *et al.* 2008; Vergili 2013). However, rejection values of DCF remain high in the neutral state, because this solute is substantially larger than the membrane pore size, and the size exclusion mechanism predominates. At high pH, the electrostatic interactions between membrane surface and DCF molecules are relevant, since both are negatively charged, and hydrophobic interactions do not occur.

However, at pH values between 4 and 6 a slight decrease in COD retention is observed for both SMX (Figure 2(b)) and DCF (Figure 3(b)) individually, which can be attributed to the simultaneous presence of the two compounds due to the contamination of the membrane with another compound, since they were also detected in HPLC analyses. This contamination can be due to the pharmaceutical molecules that were used in previous tests.

Binary pharmaceutical solutions. The speciation of SMX and DCF mixtures in aqueous solutions and their fractionation by nanofiltration is dependent on the solution pH, which also determines the charge density of the membrane surface with negative zeta potential throughout the pH range tested. In other words, the feed pH interferes with the rejection mechanisms. Thus, a pH scanning was done and the individual and global rejections were calculated with the results of HPLC (Figure 4(a)) and COD (Figure 4(b)) analysis.

As can be observed, at pH below 4 and above 7, high COD and pharmaceutical retentions are reached. Since the membrane has a negative zeta potential (is negatively charged) at high pH and the molar fraction of the negative organic species is progressively higher with increasing pH, it is expectable that the retention of the contaminants increases with increasing pH due to electrostatic repulsion.

At pH around 3, there is no electrostatic repulsion because the surface membrane is practically uncharged and both contaminants exist in neutral charged form (Simon *et al.* 2011). Thus, the predominant rejection mechanisms are size exclusion and hydrophobic interactions and since the molecular weight of SMX and DCF is higher than the membrane cut-off, the global retention is high. Moreover, as referred to previously, at low pH values, TS80 membrane is hydrophobic and SMX is hydrophilic; thus, hydrophobic interactions may also explain SMX high retentions. In turn, at intermediate pH (4–6) a decrease in COD and pharmaceutical rejection is observed, reaching

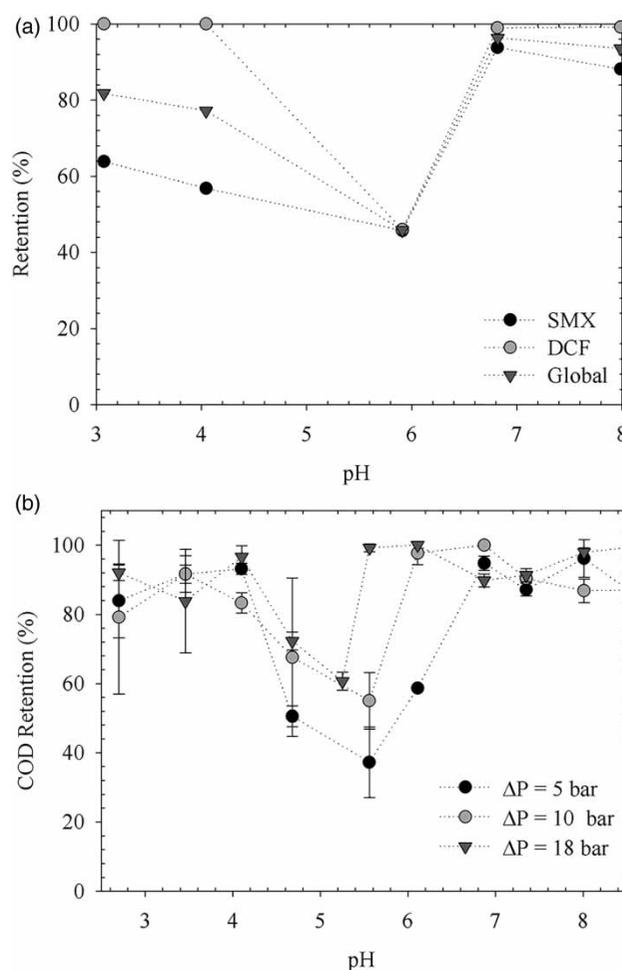


Figure 4 | Effect of the feed water pH on (a) pharmaceutical retention at 10 bar and (b) COD retention at 5, 10 and 18 bar for mixture of contaminants.

the minimal values of 37% and 46% for a pH of about 6, which is similar to the pK_{a2} of SMX, 5.8.

As mentioned previously, SMX and DCF present high individual retentions independently of the feed pH; however, when the two compounds are present simultaneously, both SMX and DCF rejection decrease, following similar profiles (Figure 4(a)). This probably occurs because there are relevant electrostatic interactions between the two compounds, which make them highly hydrophilic and with a high dipole moment, being strongly attracted to the membrane surface, passing through it.

In conclusion, multiple effects can be observed in Figure 4: a dominant charge repulsion mechanism and polarity for pH over 6, electrostatic attraction for pH between 4 and 6 and size exclusion and hydrophobic interactions for pH under 4.

The effect of feed water pH in permeate flux and, hence, in membrane permeability was also evaluated. An increase

in the membrane permeability was observed for both individual contaminants when pH increased (30.3% for SMX and 2.1% for DCF). This behavior can be due to the change in the membrane surface chemistry when solution pH is varied. The skin layer of TS80 is mostly made of polyamide material which possesses dissociable carboxylic and amine groups. At high pH values, the carboxylic groups fully dissociate and the surface gains its strongest negative charge, which favors the interactions with water molecules and makes the membrane more hydrophilic, resulting in more water molecules being permeated through the membrane pores. Additionally, the stronger electrostatic repulsion, due to higher charge density of the membrane surface, at high pH could result in the increase in the average pore size (pore swelling) (Dalwani *et al.* 2011). However, a decrease in membrane permeability of 27.06% with pH increase was observed for the mixture. This occurs probably due to higher retention of pollutants at high pH, leading to their accumulation on the membrane surface, which induces an additional resistance in Darcy's law (Luo & Wan 2013).

Moreover, the effect of pressure on COD retention was also evaluated in the range 5–18 bar, Figure 4(b)). As can be observed, at pH below 4 and above 7, in the studied pressure range, this variable presents a reduced impact on COD retention. However, at intermediate pHs, there is an increase of COD retention with applied pressure increasing. This behavior can be related to the speciation and dissociation degree of compounds, which depends on feed pH. Moreover, the increase of pressure promotes the accumulation of the solutes along the membrane surface, and consequently an increase of membrane pore clogging. The increased clogging leads to a greater contaminant rejection, since this adherent layer acts as a secondary membrane, reducing the MWCO of the membrane (Brião & Tavares 2012; Ruby-Figueroa 2012).

Effect of natural water matrix. The river water and secondary effluent were used to assess the impact of the water matrix over contaminant rejection. For this purpose, filtered water from Mondego River and a municipal secondary effluent were used and spiked with SMX and DCF (30 mg L⁻¹ of each one). In this experiment, the NF equipment was operated in an applied pressure range of 5–18 bar and natural feed water pH, considering the previous optimization done and the approach to the natural pH for wastewater treatment processes.

Figure 5 shows the rejection of contaminants as a function of drop pressure based on COD and concentration (HPLC) measurements for synthetic effluent and natural

water matrixes. For synthetic effluent at pH 7, the rejections of COD (94.8–100%) (Figure 5(a)), SMX (95.7–98.2%) (Figure 5(b)) and DCF (95.2–98.4%) (Figure 5(c)) are high due to electrostatic repulsion between solutes and surface membrane, since both are negatively charged. However, the change of the water matrix from demineralized water to secondary effluent or river water has no relevant impact on COD and contaminant retention (Figure 5). Nevertheless, a slight decrease in NF efficiency can be justified by the presence of low concentration of NOM and inorganic ions (especially Ca²⁺ and Mg²⁺) in the river water and secondary effluent, which interfere with the separation process (Table 1).

Moreover, several literature studies (Bellona & Drewes 2005; Nghiem *et al.* 2006; Verliefe *et al.* 2008) have reported that the presence of high concentrations of divalent ions in the water matrix seems to reduce the thickness of the electric double layer at the membrane surface and shield the membrane charge. This shielding leads to a decrease in electrostatic interactions with charged species, which results in a rejection decrease of negatively charged solutes by negatively charged membrane surfaces, due to the absence of electrostatic repulsion (Nghiem *et al.* 2006; Verliefe *et al.* 2008). Moreover, the deposition of positively charged NOM molecules present in natural water on the membrane surface could possibly lead to a decrease of the negative charge of the membrane surface, which reduces the electrostatic repulsion (Xu *et al.* 2006). Additionally, several authors (Bouranene *et al.* 2007; Escoda *et al.* 2010; Luo & Wan 2011) reported that there is a partial dehydration of the solute molecules in the presence of salt ions because water would preferentially solvate ions (inorganic ions captures the bound water around molecules), thus leading to a thinning of the hydration layer around solute molecules (salting-out), and consequently a decrease in the effective size of the solutes, which promotes their passage through the membrane pores.

An important issue related to the contamination of the natural water resources with pharmaceuticals is their potential toxic character and consequent impact on ecosystems, if directly released into the environment. Thus, the evaluation of the toxicity of the raw effluents and treated samples is very important. To assess the effect of the water matrix on treated effluent toxicity, the acute toxicity was evaluated by LUMISTox bioassays and results are presented in Figure 6. As can be observed, the toxicity of untreated effluents is not significantly affected by the matrix, which means that it is essentially due to the PhACs. Moreover, the change of the water matrix from synthetic effluent to secondary effluent

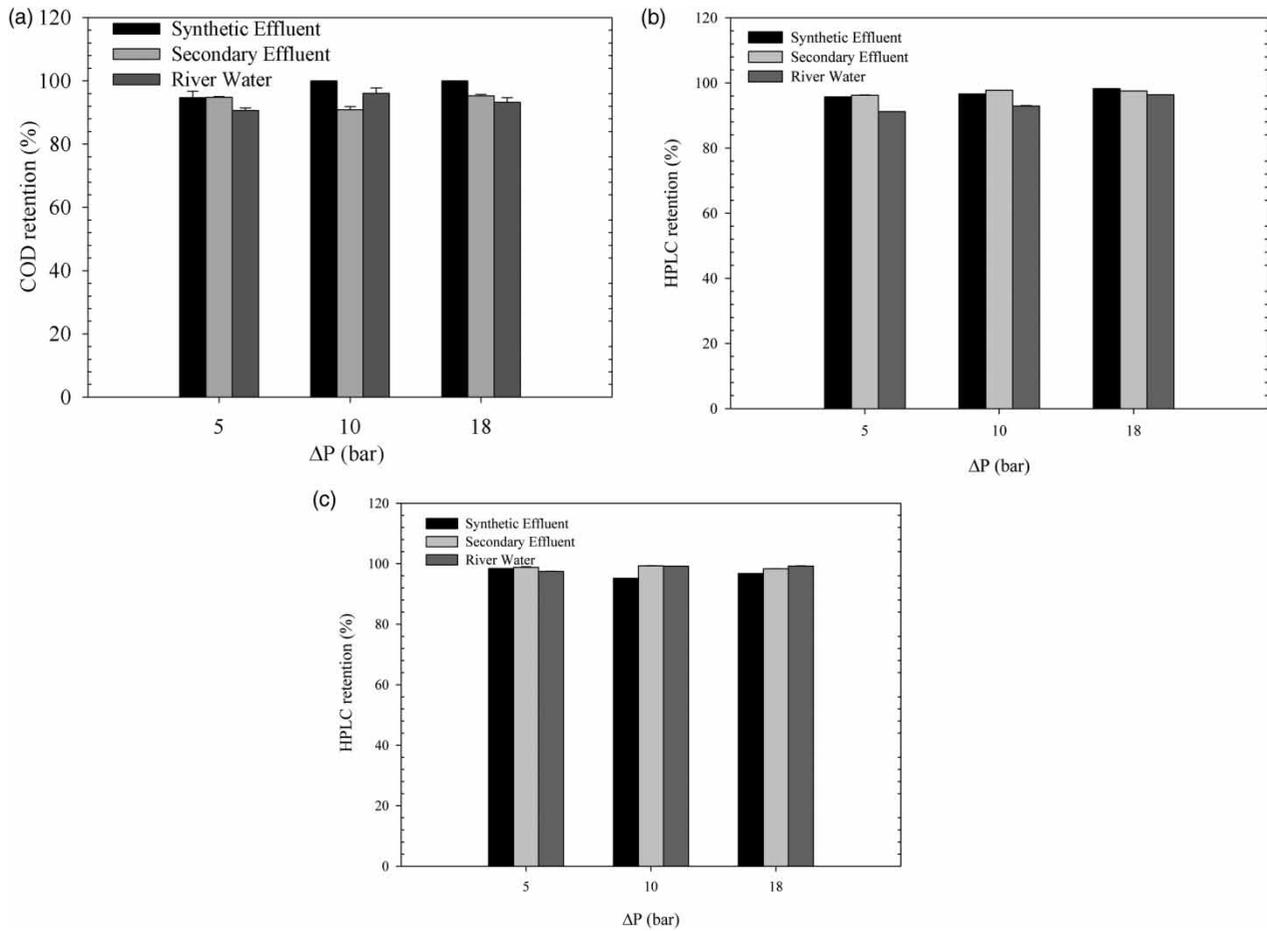


Figure 5 | Retention of (a) COD, (b) SMX and (c) DCF spiked in different water matrixes and as a function of applied pressure at pH 7.

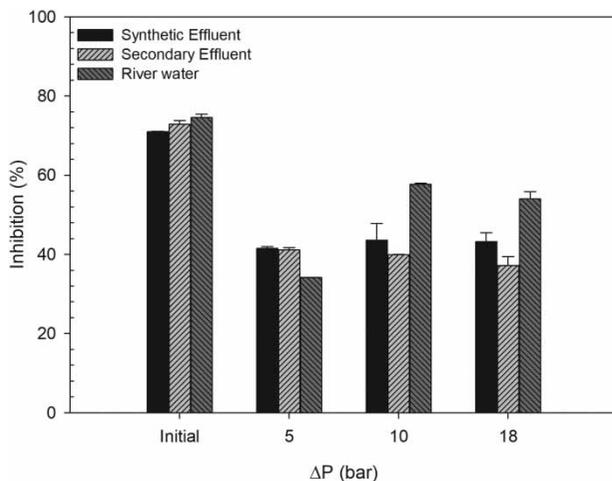


Figure 6 | Results of LUMISTox tests for the inhibition caused to *Vibrio fischeri* when exposed for 30 min to the raw effluent and treated samples taken during the nanofiltration of synthetic effluent, river water and secondary effluent.

has no relevant impact on treated samples' toxicity. However, when the river water is treated at 10 and 18 bar,

toxicity is significantly higher compared to other used matrixes probably due to a higher entrainment and permeation of inorganic ions such as Cl^- , NO_3^- , NH_4^+ and SO_4^{2-} existing in the river water and whose accumulation may have a toxic effect on the bacteria.

Analysis of membrane fouling

Since fouling is an inevitable phenomenon during membrane filtration, it has been the subject of many investigations over the last years. The main disadvantage of membrane fouling is a decline in permeate flux due to pore blocking, thus increasing costs to operate the system. Moreover, recent investigations have also revealed that the fouling can alter the performance of the separation process, and depending on the type of fouling, it results in increase or decrease of the contaminant retention (Simon *et al.* 2013a, 2013b).

Therefore, in this section the membrane fouling study performed in this work is presented. For this purpose, the

membrane permeate flux was measured over time during the filtration both of demineralized water and synthetic effluent (spiked with 30 mg L^{-1} of each contaminant) at 10 bar. In the initial stage a flux decline was observed, which reached the stable state after a few minutes. The synthetic effluent led to a more severe initial permeate flux decline (30.68%) in comparison to that caused by demineralized water (26.97%). Moreover, the permeate flux of synthetic effluent is lower, which can be due to contaminant adsorption on the membrane and pore blocking, or the concentration polarization (CP) phenomenon caused by convective transport and selective permeability. When CP increases, the effective driving force and, consequently, the permeate flux would go down (Luo & Wan 2011).

Atomic force microscopy analysis was performed for the fresh and used membrane, since this is a very useful tool for analysis of the effects of the operating conditions on the internal porosity of the membrane. In Figure 7, it is possible to see the comparison between the topographic images of both membranes. These two images are corrected to the same average, which means that the same color represents the same topographic height.

After 40 hours of operation with synthetic effluent and natural water, it is possible to conclude that the contaminants and NOM adsorbed on the membrane surface, since the membrane height (zed quota) is higher for the used membrane. The roughness based on $5 \mu\text{m} \times 5 \mu\text{m}$ surface topography images was also calculated for both virgin and used membrane. The average roughness for the virgin membrane is 22.07 nm, while for the used membrane after

40 hours' work it is 27.22 nm. These results corroborate that the used membrane has adsorbed material on it.

The inevitable presence of membrane fouling and its consequences can be overcome by a periodic chemical cleaning. Several authors (Simon *et al.* 2012) have investigated the impact of chemical cleaning on the contaminant rejection and membrane properties. In this paper, two types of cleaning (demineralized water and acid cleaning) were studied and their effect on membrane permeability and FI (Equation (1)) was evaluated and results are presented in Figure 8.

$$FI = \left(1 - \frac{L_{p,j}}{L_{p,0}} \right) \quad (1)$$

where $L_{p,0}$ is the permeability of the virgin membrane and $L_{p,j}$ is the permeability of the membrane after each wash.

Analyzing Figure 8, it is possible to verify that acid cleaning leads to a gradual decrease in membrane permeability from $1.864 \times 10^{-6} \text{ m s}^{-1} \text{ bar}^{-1}$ to $9.8 \times 10^{-7} \text{ m s}^{-1} \text{ bar}^{-1}$, which corresponds to an increase in the FI of about 47.4%. This can be due to the fact that this cleaning was not fully efficient, contributing to the continuous deposition of organic contaminants on the membrane surface and blocking its pores. Moreover, Simon *et al.* (2012) verified that membrane cleaning with citric acid (pH 2.5) led to a reduction in permeate flux of about 14% due to the decrease in interactions among the ionizable functional groups of the membrane matrix, resulting in the tightening of the membrane pores.

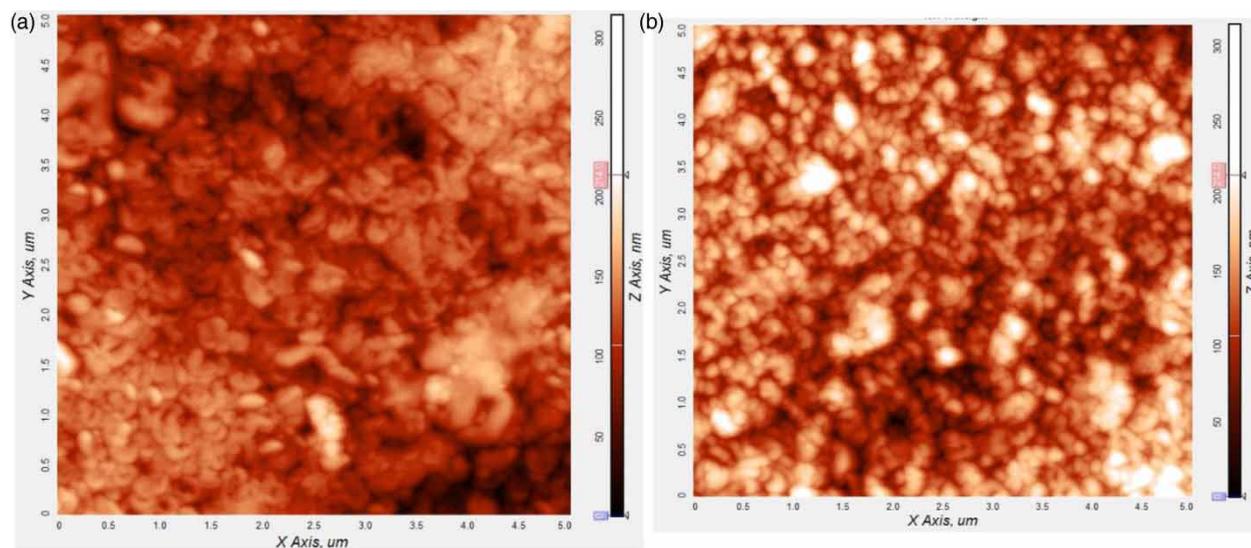


Figure 7 | Surface topography images ($5 \mu\text{m} \times 5 \mu\text{m}$) with corrected average for (a) the virgin membrane and (b) the used membrane (approximately 40 hours).

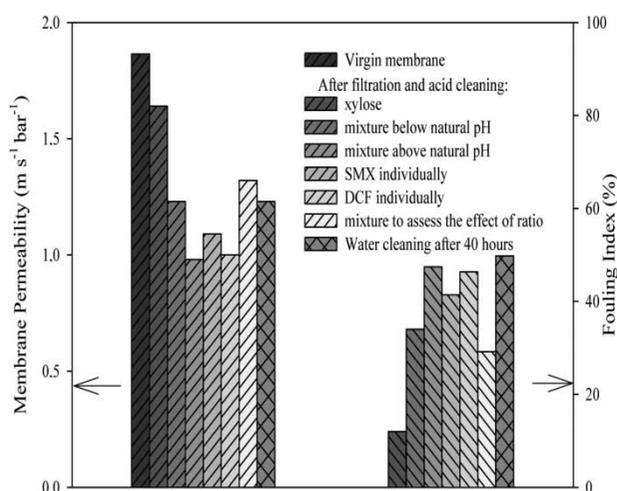


Figure 8 | Evaluation of the membrane permeability and fouling index during different trials using acid cleaning and comparison with water cleaning.

However, after the trials to assess the effect of the ratio between contaminants' concentration, an increase in membrane permeability (FI = 29.2%) is observed, which can be explained by the high state of membrane degradation due to the large number of operating hours. Regarding cleaning with demineralized water, after 40 hours of operation, an FI of 49.8% was observed, which indicates that the type of cleaning practically does not influence the final FI of the membrane.

CONCLUSIONS

The main purpose of this paper was to study and optimize the TS80 nanofiltration membrane efficiency for the removal of a mixture of SMX and DCF from water streams. Feed water pH was the operating variable that most affected contaminant rejection and membrane permeability, since it influences the membrane and solute properties and, hence, the dominant rejection mechanisms. For individual contaminants, rejections were high and not affected by feed pH. Regarding the mixture, at pH below 4 and above 7, high retentions were reached by size exclusion and electrostatic interactions, respectively. However, at intermediate pH (4–6) a decrease in COD and global contaminant rejection was observed, reaching the minimal values of 37% and 46% at pH 6, possibly due to relevant electrostatic interactions between the two compounds, which make them highly hydrophilic and with a high dipole moment.

An applied pressure of 10 bar and pH 7 were determined as the best operating conditions. At these conditions, for the synthetic effluent, an almost total COD retention and a global contaminant rejection of 96.3% were achieved. For the same conditions, the use of natural water matrixes had no significant impact on the process efficiency, with a COD retention of 90.9% and 96.1% for secondary effluent and river water, respectively. Regarding HPLC analyses, a global retention of 98.5% and 96% were achieved for the secondary effluent and river water. Moreover, nanofiltration was able to reduce the acute toxicity of both matrices towards *Vibrio fischeri*; however, the light inhibition percentage for the treated samples was higher for the river water.

AFM analysis revealed the increase of zed quota and roughness of the membrane with its use. Moreover, a higher flux decline was obtained for the synthetic effluent, which indicates the deposition of the PhACs on the membrane surface. A similar maximal FI was attained for both water and acid cleaning, 49.8% and 47.4%, respectively. The obtained results reveal that the nanofiltration is an efficient technology to remove the mixture of SMX and DCF from aqueous solutions and proved to be an effective method for the reduction of the toxicity of these contaminated effluents; however, its main drawback is the membrane fouling.

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