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Operating conditions and membrane selection for the removal of conventional and emerging pollutants from spring water using nanofiltration technology: the Tula Valley case

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ABSTRACT

The aquifer of the Tula Valley in Mexico is recharged by the infiltration of wastewater used for agricultural irrigation. This aquifer is considered to be a possible source of water for Mexico City, and although, in general, the water is good quality it still contains hardness and specific emerging pollutants. This research aims to identify a suitable treatment process based on membrane nanofiltration as it is a proven technology. Four nanofiltration membranes were compared using the critical flux concept in order to select the two that produced the largest amount of permeate. Membrane fouling was assessed by investigating the deposition of calcium using SEM images. To control hardness scaling, pretreatment with 150% of lime was employed. Finally, one membrane was selected based on its capability to remove carbamazepine, bisphenol A, triclosan, butilbenzylphthalate, and 4-nonylphenol. The selected membrane was operated at 800 kPa, producing 87.30 l m^{-2} h^{-1}.

Keywords: Critical flux; Drinking water; Fouling; Nanofiltration; Unintentional water reuse; Emerging pollutants

1. Introduction

In Mexico, the reuse of domestic wastewater for agricultural irrigation is a common practice, resulting in the final disposal of wastewater to the soil. This practice started in the late eighteenth century, when all of the wastewater from Mexico City began to be sent to the Tula Valley. In 1920, an irrigation district was built in this valley, which over time became the largest area in the world using untreated wastewater for irrigation. As a result of wastewater infiltration, an important aquifer has been formed, which is now a possible future source of water for Mexico City. The over-recharge of this aquifer has lead to the upwelling of springs, such as the "Cerro Colorado" spring which, alone, produces 600 l s^{-1} (51,840 m^3 d^{-1}). However, previous studies by Gibson et al. showed that, due to its origin, this water contains emerging contaminants (ECs); this increases the need to define a treatment process that ensures the removal of these pollutants [1]. The pre-selected treatment was nanofiltration, based on studies by Aguilar et al. [2]. This is a suitable process as it produces high quality permeate, removes natural organic matter (NOM), and retains compounds with a similar molecular weight to most of

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the ECs [3,4]. As fouling is one critical problem when using membrane processes, it is important to establish the optimum operating conditions to minimize it while still achieving acceptable permeate production. Therefore, the aims of this research were: (a) to apply the critical flux concept to determine the operating conditions to reduce fouling for treatment of water from the Cerro Colorado spring; (b) to establish the optimal conditions of softening pretreatment in order to reduce the concentration of multivalent ions in the feed water; and (c) to evaluate the removal efficiency of physicochemical contaminants (i.e. inorganic ions, total organic carbon and turbidity) and some relevant emerging pollutants.

2. Materials and methods

2.1. Spring water sampling and characterization

The water for the study was obtained from the Cerro Colorado spring, located in central Mexico at the coordinates latitude N 20°07′13″, longitude W 99° 15′43″. Samples were taken periodically, and physicochemically characterized using standard methods [5]; similarly, the concentration of the five ECs studied was determined in the spring water (Table 1), each time a sample was taken. These five pollutants were selected using the following criteria: (a) they are all contained in the spring water studied [1] and proper analytical methods for their analysis and quantification at ng l^{-1} levels are available, (b) harmful effects related to exposure to these contaminants at trace levels, notably endocrine disrupting effects in aquatic organisms, have been widely demonstrated [6,7], and (c) the selected compounds have differences in both their physicochemical properties and chemical structure (Table 2); for this reason, differences in the behaviour of each compound may be expected throughout the nanofiltration process and the results obtained might be extrapolated for other pollutants with similar characteristics.

2.2. Fouling potential of water

To evaluate the fouling potential of the water SDI, MFI and LSI tests were performed. These tests are explained in the sections below.

2.2.1. Silt density index (SDI)

This consisted of recording the time for filtration of 500 ml of the spring water studied (t_i) through a 0.45 μm nitrocellulose filter, at 30 psi (~200 kPa). After 15 min (t), a second 500 ml sample of the same water was filtered recording the filtration time in order to apply Eq. (1). SDI values between 0 and 3 is recommended for nanofiltration processes according to Park et al. [10].

$$\mathrm{SDI} = \frac{\left[1 - \frac{t_i}{t_f}\right]}{t} \times 100 \tag{1}$$

Table 1
Characterisation of Cerro Colorado spring water and comparison with local and international standards

Parameters	Cerro Colorado spring water	US EPA[1], 2002	WHO[2], 2004	Standards in Mexican laws
AUV_{254} (cm^{-1})	0.06 ± 0.001	–	–	–
DOC (mg l^{-1})	2.6 ± 0.1	–	–	–
TDS (mg l^{-1})	1127 ± 43	500.0	600–1000	1000.0
Conductivity (mS cm^{-1})	1754 ± 45	–	–	–
Turbidity (NTU)	0.71 ± 0.05	0.3	<5	5.0
pH	7.7 ± 0.5	6.5–8.5	6.5–8.0	6.5–8.5
Alcalinity (mg l^{-1} as $CaCO_3$)	537 ± 5.8	–	–	–
Total hardness (mg l^{-1} as $CaCO_3$)	401 ± 4.6	–	100–200	500.0
Ca^{2+} hardness (mg l^{-1} as $CaCO_3$)	275 ± 7.6	–	–	–
Carbamazepine (ng l^{-1})	7.7 ± 1.3	–	–	–
Bisphenol-A (ng l^{-1})	0.4 ± 0.2	–	–	–
Triclosan (ng l^{-1})	1.3 ± 0.2	–	–	–
Butylbenzylphthalate (ng l^{-1})	2 ± 0.4	–	–	–
4-Nonylphenol (ng l^{-1})	8 ± 2	–	–	–

[1] [8].
[2] [9].

2.2.2. *Modified fouling index (MFI)*

The MFI test was performed using the same apparatus as the SDI. The filtered volume was recorded at intervals of 30 s over a total period of 15 min. The MFI is the slope of the curve of the inverse flow (1/*Q*) versus the cumulative volume filtered (*V*), as expressed in Eq. (2). An MFI value of <10 s l^{-1} is suggested for nanofiltration processes by Park et al. [10].

$$\frac{1}{Q} = a + \mathrm{MFI} \times V \tag{2}$$

2.2.2.1. Langelier saturation index (LSI). This index is used to predict the scaling potential of feed water by precipitation of divalent ions, measured as calcium carbonate ($CaCO_3$). The calculation of this index is carried out using Eq. (3):

$$\mathrm{LSI} = \mathrm{pH}_{fw} - \mathrm{pHs} \tag{3}$$

where $\mathrm{pH_{fw}}$ is pH of the feed water and $\mathrm{pH_S}$ is saturation pH for $CaCO_3$. An LSI value >0 implies that the water will cause scaling. Beneath this value the water tends to be corrosive.

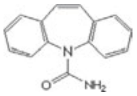
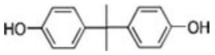
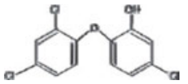
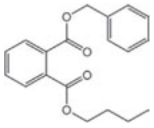
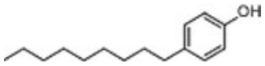
2.3. *Nanofiltration membranes*

Four different nanofiltration membranes were pre-selected (Table 3) based on the characteristics provided by the manufacturer and the characteristics of the water tested.

2.3.1. *Membrane characterisation*

2.3.1.1. Permeability with pure water (PWP). Membranes were characterised in terms of their PWP using distilled water. Before the test, membranes were stored at 4°C in distilled water for a minimum of 24 h. Subsequently, the pure water was filtered using four different ascending and descending pressures (20 min for each pressure), and a volume of permeate was collected. The transmembrane pressure (TMP) in the cell is the average of the pressure in the feed and concentrate lines, as

Table 2
Physicochemical properties of the emerging pollutants studied

Compound	Chemical structure	Molecular weight (g mol^{-1})	pK_a[1]	pK_{ow}[2]	Water solubility (mg l^{-1})[3]
Carbamazepine		236	13.9	2.3	18
Bisphenol-A		228	9.8	3.4	120
Triclosan		289	8.4	4.8	9.6
Butylbenzylphthalate		3112	–	4.9	0.26
4-Nonylphenol		220	10.3	4.5	5.4

[1] Acidic ionization coefficient.
[2] Octanol–water coefficient.
[3] At 25°C.

Table 3
Nanofiltration membranes characteristics

Membrane	Molecular weight cut-off (Da)	Operating temperature (°C)	Maximum operating pressure (kPa)	Operating pH	Maximum SDI_{15}
TFC-SR3 (Koch)	200	5–50	4140	3–10	5
NF-90 (Dow)	200	<45	4100	2–11	5
NF-270 (Dow)	200	<45	4100	2–11	5
302986 (Thomapor)	100	<50	5000	4–11	5

expressed in Eq. (4). The permeate flux was calculated using Eq. (5), as proposed by Boerlage et al. [11]:

$$\text{TMP} = \frac{P_{feed} + P_{conc.}}{2} \tag{4}$$

$$J = \frac{\eta_T}{\eta_{20^\circ C}} \frac{Q}{A\Delta P} \tag{5}$$

where η_T is the water viscosity at the operating temperature; $\eta_{20^\circ C}$ is the water viscosity at 20°C; Q is the clean water flow at the operating temperature ($m^3\ s^{-1}$); A is the membrane area (m^2); and ΔP is the pressure difference (kPa). Finally, the PWP is the slope in the curve represented by the relationship of J ($l\ m^{-2}\ h^{-1}$) and TMP as showed in Eq. (6):

$$J = PWP \times TPM \tag{6}$$

2.3.1.2. Contact angle. This is a measure of the wettability of a solid surface. It corresponds to the angle formed by the tangent to the liquid–gas interface and the plane formed by the solid (membrane) in a contact solid–liquid–gas. It gives an idea of the membrane surface hydrophobicity. To determine it, an optical microscope was used to observe the projected image of a 5 µl drop of distilled and spring water.

2.3.1.3. Critical flux. This was calculated by plotting the flux (J) against the transmembrane pressure (TMP) profile. The latter was determined when the flux was decreased keeping the pressure constant. The plotted profiles were analyzed according to the method proposed by Espinasse et al. [12], alternating positive and negative pressure changes.

2.4. Pretreatment selection

To reduce the multivalent ions causing the hardness (mainly Ca^{2+} and Mg^{2+}), a pretretament with lime softening was chosen. To select the optimal dose of lime, seven 1 l spring water samples were used. A different lime dose was applied to each one within a range of 0% to 180% (30%, 60%, 90%, 100%, 120%, 150% and 180%) of the stoichiometric dose calculated to neutralize the total hardness. Subsequently, each sample was filtered and the supernatants were collected to determine total hardness, as well as calcium and magnesium hardness, alkalinity and pH. The tests were repeated five times.

2.5. Removal of conventional parameters and emerging contaminants (EC)

After selecting the pretreatment conditions for the feed water and for the nanofiltration proceess, the removal efficiency for conventional parameters and ECs was studied. For the determination of EC removal, samples of 20 l were spiked with carbamazepine, 4-nonylphenol, triclosan, bisphenol-A and butylbenzylphthalate, at concentrations of: 287, 1502, 59.2, 73 and 171 ng l^{-1}, respectively, prior to filtration. Three litres of permeate were collected, in triplicate, in amber glass bottles and stored at 4°C overnight, until analysis the following day. It was decided to perform analysis only for the permeate of NF-270 and TFC-SR3 in three runs for each membrane. For the TFC-SR3 membrane, the influent water was not previously softened, in order to observe differences in the rejection of ECs due to the reduction of hardness.

2.6. Emerging pollutants quantification

The analysis of the emerging pollutants was carried out using the methodology described by Gibson et al. [1]. Briefly, 3 l of raw water or permeate were filtered through a 0.45 µm nitrocellulose filter and the surrogate standards were added (100 ng of 4-*n*-nonylphenols 100 ng of 3,4-D and 100 ng of 10,11-dihydrocarbamazepine). Samples were stabilized at pH 2.0 and then passed through OASIS HLB cartridges (Waters, MA, USA) preconditioned with acetone (2 × 5 ml) and 5 ml of 10% acetic acid solution. Carbamazepine was eluted with 5.5 ml of 40:60 acetone:sodium bicarbonate 0.1 M buffer (pH 10), while the phenols and butylbenzylphthalate were eluted with 6 ml of acetone. Water was removed from samples in both phases using anhydrous sodium sulphate and the internal standards (100 ng of clofibric acid, 100 ng of [$^2H_4$] 4-*n*-nonylphenol and 100 ng of [$^2H_4$] DEHP) were added. Derivatization was carried out using the reagent MTBSTFA (Sigma-Aldrich) for carbamazepine and BSTFA (Sigma-Aldrich) for both phenols and butylbenzylphthalate, and heating at 60°C for 30 min. In addition, laboratory blanks were carried out and the concentrations determined in these blanks were subtracted from those detected in the samples. Analysis was performed using a HP-6890 gas chromatograph coupled to a HP5-MS fused silica column (30 m × 0.25 mm and 0.25 mm of film thickness). Injection was done in splitless mode at 250°C; helium was the carrier gas at 1 ml min^{-1} and the oven program was 100°C for 1 min, 20°C min^{-1} to 280°C and 280°C for 10 min. The quantification was done using a HP 5973 mass selective detector; electron impact source temperature was 230°C and the electron energy of 70 eV. The quadrupole temperature was 150°C and the single ion monitoring (SIM) mode was used for quantitative analysis. Recoveries obtained for the surrogate standards were between 95% and 97% for 4-*n*-nonylphenol and 10-11, dihydrocarbamazepine, respectively, and around 75% for 3,4-D.

2.7. Apparatus

Tests to determine the fouling potential of water (SDI, MFI) were carried out using an OSMONICS AutoSDI device, which records flow and filtration times and calculates the SDI according to the ASTM-D4189 standardized method. The MFI calculation was performed

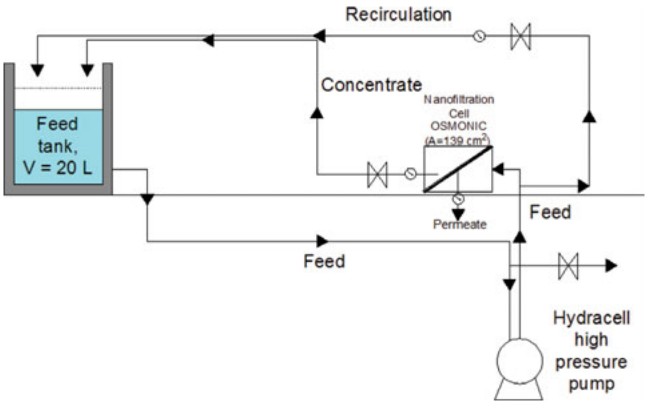


Fig. 1. Nanofiltration experimental module.

manually with the data supplied by the device. The membranes' pure water permeability (PWP) was tested in a filtration unit (Sepa II, GE OSMONICS, Minnetonka, MN), with an effective area of permeate of 139 cm^2, operated in batch mode. The nanofiltration experimental module consisted of a 20 l feed tank and four flow lines: feed, recirculation, concentrate, and permeate (Fig. 1).

For determination of total organic carbon (TOC) and UV absorbance at 254 nm wavelength, a DR 5000 HACH spectrophotometer was used. pH, conductivity and SDT were measured with a multiparameter SENSION 156 HACH instrument. Turbidity was analyzed with a HI 93703-11, HANNA turbidimeter.

3. Results and discussion

3.1. Cerro Colorado spring water characterisation

In general, the quality of the Cerro Colorada sping met most of the criteria to be considered for drinking water. However, this water is very hard (>300 mg l^{-1} CaCO$_3$). Previous work has shown the presence of multivalent ions (notably Ca^{2+} and Mg^{2+}), and their interaction with NOM is one of the causes of membrane fouling [13,14]. However, concentrations of the selected ECs in the feed water were of the order ng l^{-1} (Table 1).

3.2. Fouling potential of water

The SDI calculated was 5.8 (i.e., higher than that specified for each membrane) (Table 3). The MFI was 2.92 and was within the recommended range for nanofiltration. However, it was observed that the transition of the cake filtration zone to the compaction zone occured quickly, indicating a very rapid end of the production cycle. The LSI value was 3.8, showing that the Cerro Colorado water is highly scaling. In summary, the results of all these tests indicated that the water characteristics can cause fouling or scaling. Moreover, the LSI result illustrates the need for softening pre-treatment in order to reduce mechanical damage and clogging of the membrane.

3.3. Membrane characterisation

3.3.1. Permeability with pure water

PWP values obtained (Table 4) are consistent with those obtained by other authors working with water under similar conditions [15,16].

3.3.2. Contact angle

It is known that less permeable membranes have a larger contact angle. Membranes 302986 and TFC-SR3, with the largest contact angles, presented low values of PWP (Table 4).

3.3.3. Critical flux

For the NF-90 and TFC-SR3 membranes, the critical flux with Cerro Colorado water was determined experimentally (Fig. 2). On the other hand, critical flux could not be detected at the pressure range of the test for the NF-270 and 302986 membranes. This suggests that within this pressure range, no irreversible fouling will occur quickly. Membrane NF270 had the better water production within the range of pressures evaluated.

In order to validate the measured critical flux, two filtration runs using the NF-90 and TFC-SR3 membranes, below and above critical flux, were performed. After 6 h of filtration, images were obtained using a scanning electron microscope (SEM) (JEOL JSM-5600 LV with 300,000× magnification) to evaluate the surface membrane fouling and/or scaling (Fig. 3). When the operation was

Table 4
Results for the characterisation of the membranes

Membranes	PWP (l m^{-2} h^{-1} bar^{-1})	Contact angle with pure water	Critical flux (l m^{-2} h^{-1})	Critical pressure (kPa)	Pressure range tested (kPa)	Operating flux (l m^{-2} h^{-1})
NF90	12.24	29 ± 1.97	69.5 ± 4.1	634 ± 14	270–930	<69.5
NF270	17.21	29 ± 3.21	–	–	250–830	87.8
TFC-SR3	4.77	37 ± 1.0	56.9 ± 2.8	1255 ± 7	250–1650	<56.9
302986	2.89	35 ± 3.37	–	–	250–900	22.4

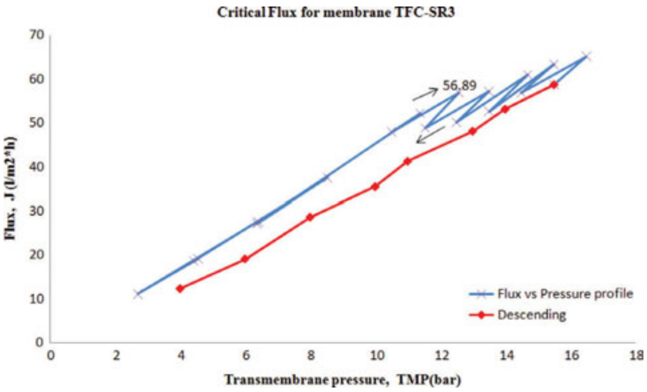


Fig. 2. Critical flux measurement for TFC-SR3.

performed below the critical flux, a flux decline was not observed over the short term (6 h), neither was scaling due to divalent ions, even when raw water (i.e. unsoftened) was filtered. For the qualitative assessment of the compounds present in the fouled membrane, the SEM was used with a suitable X-ray detector (EDS, energy dispersive spectroscopy). The micrographs revealed, for both membranes, that calcium was the main component of fouling (Fig. 3(d)). This is a scaling product resulting from the hardness of feed water and highlights the benefits of operating below the critical flux.

3.4. Pretreatment

Calcium and magnesium were removed with softening, using slaked lime to precipitate calcium carbonate and magnesium hydroxide. The stoichiometrical lime dose to neutralize the hardness of the Cerro Colorado spring water was 737 mg l^{-1} as $Ca(OH)_2$. When a dose of 150% of lime was used, the minimum value of total hardness achieved was 21.2%. Doses above 150% resulted in a notable increase of total hardness. Regarding calcium hardness, the minimum value obtained was 21.7% of the initial value at the 120% lime dose. Above this dose, calcium hardness again increased. Calcium concentration decreased rapidly at the 30%, 60% and 90% doses of lime. After this, there was no significant change in concentrations up to 120%. Optimal removal of calcium was achieved at a dose of 90% lime. At this point, the ideal pH to precipitate calcium carbonate hardness, approximately 9.5, was reached. For magnesium hardness, maximum removal was achieved with a lime

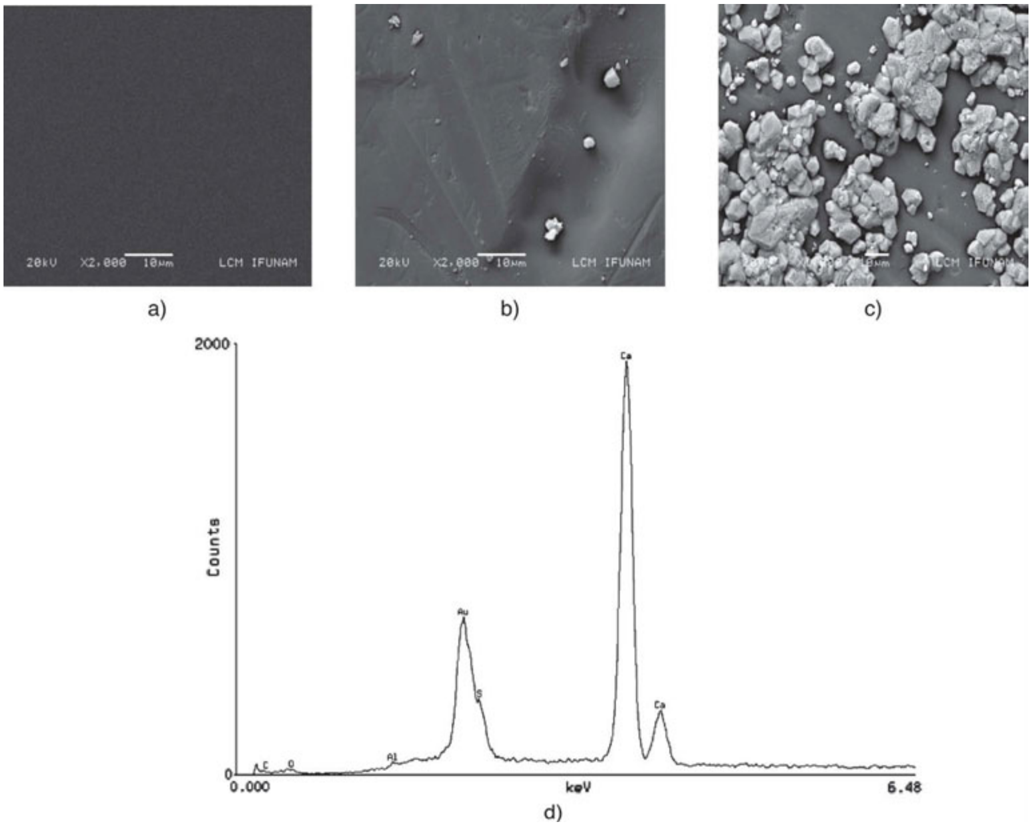


Fig. 3. SEM images of (a) clean TFC-SR3 membrane, (b) used TFC-SR3 membrane below critical flux, (c) used TFC-SR3 membrane over critical flux, and (d) EDS spectrum of the foulants on TFC-SR3 membrane surface.

dose of 150%. Using a dose of lime of 150%, alkalinity decreased from 520 mg l^{-1} (as $CaCO_3$) to 168 mg l^{-1}. Higher doses (up to 180%) increased alkalinity to up to 240 mg l^{-1} (as $CaCO_3$). This is explained because after reaching the optimal dose of lime, free OH-ions were released, increasing alkalinity.

When filtration using unsoftened and softened water was carried out for the membranes NF90, NF270 and 302986, an increase in flux was observed at the same pressure for softened water, due to the reduction of Ca^{2+} and Mg^{2+} ions, both responsible for the loss of permeate flux.

3.5. Pollutants removal efficiency

For conventional parameters, the produced permeate was in line with international regulations for drinking water; while removal of the five ECs using only membranes NF 270 and TFC-SR3 was above 90% (Table 5).

Previous studies, focused on the removal of ECs (mainly endocrine disrupting chemicals) by means of membrane processes, report rejection efficiencies over a very wide range, from 10% to 99.9% [17]. Chang et al. reported removals for endocrine disrupters up to 95% using a nanofiltration process, with efficiencies depending on the chemical properties of the contaminants and the membrane characteristics [18].

For both membranes, butylbenzylphthalate was the main compound removed, probably due to the higher molecular weight and size of the molecule. Butylbenzylphthalate is highly hydrophobic (*see* Table 2), and sorption onto the membrane was also posible. The higher removal percentages with the TFC-SR3 membrane, which showed the largest contact angle, suggests that hydrophobicity plays an important role in the removal of the emerging organic pollutants. Carbamazepine showed a similar behaviour. This compound remained in its non-ionized and hydrophobic state, favouring its retention on the membrane. In contrast, at the pH value of the tested water (7.7), 4-nonylphenols, bisphenol-A and triclosan showed a different level of ionization (0.25%, 1% and 16.6%, respectively) and wereremoved to a lesser extent than carbamazepine and butylbenzylphthalate. Low removal of dissolved organic carbon using both NF-270 and TFC-SR3 membranes indicated that as ionization increased, lower retention on the membranes was observed for different compounds. Nevertheless, this is not completely true for bisphenol-A, which despite being slightly ionised, passed through the membranes. For this compound it appeared that that its solubility in water significantly affected its removal efficiency.

Other water treatment process, such as flocculation, coagulation, and precipitation have been demonstrated to be less efficient at removing compounds with molecular weights less than 500 Da [19]. Other membrane processes such as ultrafiltration and microfiltration are not suitable for the treatment of these pollutants [20] unless they are coupled with other processes such as adsorption, biodegradation or catalysis. In addition, the results showed that the nanofiltration process was efficient at removing the antiepileptic drug carbamazepine, which is a compound highly recalcitrant to many different treatement procedures.

No effect of softening on the removal of ECs was observed. This is consistent with data obtained by

Table 5
Removal efficiencies for each parameter in the permeates (%)

Parameter	Membranes			
	NF-90	NF-270	302986	TFC-SR3
Total hardness	95.0 ± 5.3	91.9 ± 3.1	90.4 ± 5.0	92.85 ± 4.6
Ca^{2+} hardness	99.0 ± 1.15	96.4 ± 0	96.4 ± 0.0	94.4 ± 1.2
Mg^{2+} hardness	86.2 ± 6.43	81.9 ± 3.1	77.2 ± 5.0	89.9 ± 0.6
Alkalinity	93.91 ± 1.15	89.6 ± 2.0	78.5 ± 2.3	76.2 ± 4.0
Total dissolved solids	96.3 ± 2.8	77.9 ± 14.9	94.2 ± 23.3	75.8 ± 3.8
Dissolved organic carbon	68.4 ± 2.82	68.4 ± 0.05	78.95 ± 0.03	68.4 ± 0.02
AUV_{254}	100	46.6 ± 0.0	91.4 ± 0.0	77.6 ± 0.0
Turbidity	87.3 ± 0.03	77.5 ± 0.0	88.7 ± 0	45.1 ± 0.8
Carbamazepine	–	97.2 ± 0.3	–	98.7 ± 0.3
4-Nonylphenols	–	95.9 ± 1.3	–	97.3 ± 1.4
Triclosan	–	93.7 ± 1.0	–	95.4 ± 3.2
Bisphenol-A	–	91.8 ± 0.6	–	90.4 ± 0.7
Butilbenzylphtalate	–	98.4 ± 0.4	–	99.7 ± 0.5

Bolong et al. [3], which indicated that the removal of these pollutants using lime softening is very low (<20%). However, Comerton et al. reported a significant decrease in the rejection of endocrine disrupting chemicals and pharmaceutically active compounds in the presence of some cations [21].

4. Conclusions

Applying the critical flux concept to investigate the operating conditions of four preselected nanofiltration membranes, it was possible to select one membrane (NF 270) to potabilize the Cerro Colorado spring water. The operating conditions selected were 800 kPa and 87.3 l m^{-2} h^{-1}. To reduce the permability loss caused by hardness scaling, pretreatement using lime was applied. Nanofiltration processes were demonstrated to efficiently remove carbamazepine, bisphenol-A, triclosan, butilbenzylphthalate, and 4-nonylphenol. The first of these compounds is highly recalcitrant to many water treatment processes. Removal was increased for hydrophobic compounds as a result of their adsorption onto the membranes, while water solubility reduced the retention of bisphenol-A in the process. In addition, it was concluded that the critical flux concept is useful to select the membranes, those producing the largest amount of permeate, and to easily define the conditions that lead to reduction of fouling.

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