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Nanofiltration of surface water for the removal of endocrine disruptors

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ABSTRACT

The assessment of surface water nanofiltration (NF) for the removal of endocrine disruptors (EDs) – Nonylphenol Ethoxylate (IGEPAL), 4-Nonylphenol (NP) and 4-Octylphenol (OP) – was carried out with three commercial NF membranes – NF90, NF200, NF270. The permeation experiments were conducted in laboratory flat-cell units of 13.2×10^{-4} m^2 of surface area and in a DSS Lab-unit M20 with a membrane surface area of 0.036 m^2. The membranes hydraulic permeabilities ranged from 3.7 to 15.6 kg/h/m^2/bar and the rejection coefficients to NaCl, Na_2SO_4 and Glucose are for NF90: 97%, 99% and 97%, respectively; for NF200: 66%, 98% and 90%, respectively and for NF270: 48%, 94% and 84%, respectively. Three sets of nanofiltration experiments were carried out: i) NF of aqueous model solutions of NP, IGEPAL and OP running in total recirculation mode; ii) NF of surface water from Rio Sado (Setúbal, Portugal) running in concentration mode; iii) NF of surface water from Rio Sado inoculated with NP, IGEPAL and OP running in concentration mode. The results of model solutions experiments showed that the EDs rejection coefficients are approximately 100% for all the membranes. The results obtained for the surface water showed that the rejection coefficients to natural organic matter (NOM) are 94%, 82% and 78% for NF90, NF200 and NF 270 membranes respectively, with and without inoculation of EDs. The rejection coefficients to EDs in surface water with and without inoculation of EDs are 100%, showing that there is a fraction of NOM of high molecular weight that retains the EDs in the concentrate and that there is a fraction of NOM of low molecular weight that permeates through the NF membranes free of EDs.

Keywords: Nanofiltration; Surface water treatment; Endocrine disruptors; Natural organic matter; Drinking water; Nonylphenol ethoxylate; 4-Nonylphenol; 4-Octylphenol

1. Introduction

In the production of drinking water of high quality, the removal of conventional micropollutants such as pesticides, alkylphthalates and residual natural organic matter (NOM) has been object of particular importance and of numerous literature. Among the technologies addressing this problem, special relevance is given to membrane technologies and more specifically to pressure-driven membrane processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [1–9]). More recently, particular concern is given to the group of micropollutants designated by endocrine disruptors chemicals (EDs). They are

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natural or synthetic chemical substances present in the water environment that interfere in the endocrine system of humans and other animals, affecting their health, growth and reproduction. The EDs can be integrated in surface waters through diverse mechanisms, like direct discharge of industrial and domestic wastes, the discharge of effluents from biological treatment plants and drains of agriculture into rivers and soils. The works of Elimelech and of Schafer are important references in regard to UF, NF and RO for the removal of natural hormones in water [10,11].

In industrial activity, many chemicals like pharmaceuticals, steroids and surfactants originate upon biodegradation compounds that act as endocrine disruptors. Snyder et al. addressed the removal of the first two classes of chemicals through membrane technologies and activated carbon and González et al. addressed the degradation of surfactants through membrane bioreactors [12,13].

The process of biodegradation and incorporation of EDs metabolites in water is well documented by Ahel et al. [14,15]. Among the EDs metabolites the 4-nonylphenol (NP), the nonylphenol ethoxylate (NPE) and the 4-octylphenol (OP) are object of particular concern as they are in the list of priority substances in the field of water policy and amending Directive 2000/60/EC [16]. In fact, they have been identified in surface waters of Japan, USA, Canada, United Kingdom, Spain and Portugal [17–22]. Already in 1994 Ahel et al. reported the possibility of natural waters contamination through secondary routes, namely: 1) deposition in soil of contaminated sludges from anaerobic treatment and subsequent soil erosion; 2) re-suspension of contaminated sediments. In the treatment of surface water for the production of drinking water the re-suspension of NOM sediments would be a potential source of NP, NPE and OP contamination, as these hydrophobic compounds are preferentially sorbed by the NOM [14,15]. In fact, despite the very low water solubilities, the trace amounts of these compounds in the order of ng/l are still a matter of concern to aquatic life [12]. Therefore, the assessment of technologies for their removal requires the quantification of EDs in feed and treated streams. So, prior to any technology assessment one is faced with the fact that the detection, characterization and quantification of EDs remains still a matter of analytical chemistry concern and research [23–25].

The present work addresses both removal of NP, NPE and OP from surface water by nanofiltration and their quantification in the NF streams – feed, concentrate and permeate. Three sets of nanofiltration experiments were carried out with: i) aqueous model solutions of NP, NPE and OP and of humic acid, running in total recirculation mode; ii) surface water from Rio Sado (Setúbal, Portugal), running in concentration mode; iii) surface water from Rio Sado inoculated with NP, NPE and OP, running in concentration mode. These sets of experiments were carried out with three commercial membranes, NF90, NF200 and NG270, at different transmembrane pressures for the EDs removal optimization and the enhanced effect of NOM on EDs water solubilization. The quantification of EDs in the NF streams – feed, concentrate and permeate – was performed through Solid-Phase Extraction (SPE)/High Performance Liquid Chromatography (HPLC).

2. Experimental

The nanofiltration experiments were carried out using model solutions, containing 4-Nonylpheno (NP), 4-Octylphenol (OP) and Nonylphenol Ethoxylate (IGEPAL), and Sado river water with and without inoculation of ED – NP, OP and IGEPAL.

2.1. Materials

Commercial 4-Nonylphenol, 4-Octylphenol and Nonylphenol Ethoxylate (IGEPAL) by Sigma-Aldrich were used to prepare model solutions and to inoculate Rio Sado water. Three 5 l model solutions with 5 mg/l of NP, OP and IGEPAL were prepared, and left agitating for three days in a Vibromatic Side-Arm Extension Clamp (P. Selecta, Spain) at a rate of 250 U/min. Due to the low solubility of NP, OP and IGEPAL in water, the final concentrations in solution, determined by HPLC, were found to be 358.86 μg/l, 182.74 μg/l and 710.77 μg/l, respectively.

Commercial humic acid; HA, supplied by Aldrich Chemicals, was chosen as a model for colloidal NOM and was purified to remove iron and to decrease the ash content. The purification was performed as described by Costa and de Pinho, 2005 [26]. All humic acid model solutions were prepared with deionized water. HCl, NaOH, and NaCl, were used to adjust the pH and the ionic strength of the solutions.

For the present work, three different Nanofiltration membranes of polyamide by Filmtec were used – NF90, NF200 and NF270.

2.2. Surface water

The surface water was collected in the Sado River (Setúbal area) between May and October 2009. The water was characterized in terms of pH, conductivity, and total organic carbon (TOC). The characterization can be found in Table 1 (results section).

Table 1
Characterization of the sado river water

	Sample collected in May 18th 2009 (Monday)	Sample collected in June 18th 2009 (Thursday)	Sample collected in October 14th 2009 (Wednesday)
pH	8.1	8.1	8.1
Conductivity (mS/cm)	52.2	51.3	45.6
TOC (mg C/l)	4.870	4.630	5.006
[IGEPAL] (µg/l)	n.d	0.023	0.001
[OP] (µg/l)	n.d	0.027	0.008
[NP] (µg/l)	n.d	n.d	0.035

n.d. - not detected.

2.3. Methods

2.3.1. Membranes characterization

Before the experiments the membranes were compacted for 2 to 3 h with deionized water at a transmembrane pressure of 30 bar. The membranes were characterized in terms of pure water hydraulic permeability (L_p), salt apparent rejection coefficients (NaCl and Na_2SO_4) and an apparent rejection coefficient to a reference organic solute (Glucose). The apparent solute rejection coefficients (f), defined as $f = (C_f - C_p)/C_f$, where C_f and C_p are the feed and the permeate concentrations, respectively, were calculated in terms of total organic carbon (TOC) content for the organic solutes and in terms of conductivity for the salt solutions.

2.3.2. Permeation experiments with endocrine disruptors model solutions

The experiments with model solutions of NP, OP and IGEPAL were performed in total recirculation mode (where both permeate and concentrate are recirculated into the feed tank) in a flat-cell unit (described by Afonso and de Pinho [27]). The flat-cell unit set-up is constituted by 6 permeation cells of NF, each with a membrane surface area of 13.2 cm², Fig. 1. Three 5 mg/l model solutions were prepared and the final concentrations in solution were 710.77 µg/l of IGEPAL, 358.86 µg/l of NP and 182.74 µg/l of OP, respectively. These values are lower than 5 mg/l due to the low solubility of the ED in water. The feed circulation flowrate was 0.6 l/min and the operating pressure was 30 bar. The resulting samples of these three experiments were analyzed by HPLC.

2.3.3. Permeation of humic acid model solutions

These permeation experiments were performed at different ionic strengths (10^{-2} and 10^{-3} M) and different transmembrane pressures (10–35 bar) in a flat-cell unit (described by Afonso and de Pinho [27]).

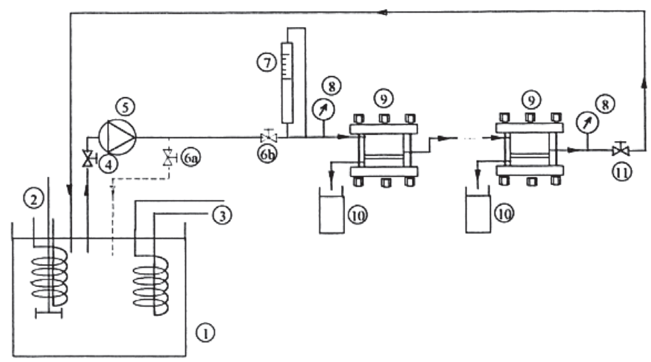

Fig. 1. Nanofiltration flat-cell unit set-up.

In the first experiment the feed tank of the flat-cell unit was charged with 5 l solution with a concentration of 10 mg/l of humic acid (HA), at a pH of 6.2 and an ionic strength of 10^{-2} M. For the second experiment the feed tank was charged with the same solution, but the ionic strength of the solution was now of 10^{-3} M. The feed circulation flowrate was 0.6 l/min and the operating pressures varied between 10 and 35 bar. The samples collected in these experiments were analyzed in terms of total organic carbon (TOC).

2.3.4. Permeation of surface water (Sado river)

The permeation experiments carried out with the surface water of Sado River envisaged the removal of the organic matter and of the endocrine disruptors (NP, OP and IGEPAL). The experiments were carried out in concentration mode and the installation used was the DSS Lab-unit M20, Fig. 2. For all of the experiments the initial feed volume was 27 l of water from the Sado River. These experiments were performed at 30 bar and 25°C. The feed solution, the permeates and the concentrates were analyzed in terms of pH, conductivity, TOC and HPLC (NP, OP and IGEPAL). The permeate flux variation with the water recovery rate (WRR) was also assessed.

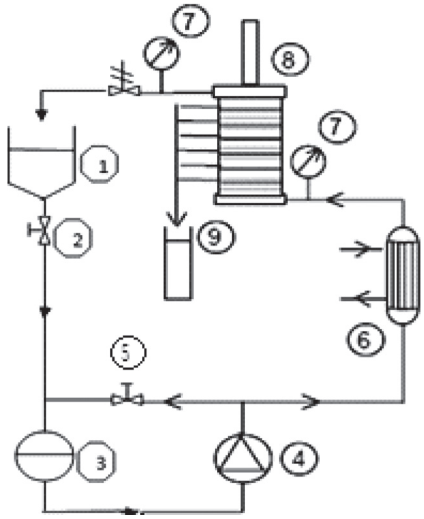

Fig. 2. Nanofiltration DSS Lab-unit M20 set-up.

Three samples of Sado River were collected on May 18th, 2009 (Monday), June 18th, 2009 (Thursday), and October 14th, 2009 (Wednesday)).

For the sample collected on June 18th two experiment sets were carried out, one with the surface water as collected, and another one, in the same day, with surface water inoculated with the EDs studied. The ED concentrations detected by HPLC after solubilization were of 0.791 μg/l IGEPAL, 0.229 μg/l of NP and 0.229 μg/l of OP.

With the sample collected on October 14th the same procedure was followed as mentioned above, and the ED concentrations detected by HPLC after solubilization were of 1.682 μg/l IGEPAL, 12.271 μg/l of NP and 12.271 μg/l of OP.

2.4. Membrane cleaning

At the end of each experiment the membranes were cleaned with deionized water, at a maximal flowrate, and a minimal pressure, until 90% of the initial hydraulic permeabilities were reached.

2.5. Determination of the concentration of NP, OP and IGEPAL

2.5.1. Extraction

The aim of this stage was the concentration of the compounds NP, IGEPAL and OP, as well as their separation from species that could interfere with the analysis. The extraction of these compounds was performed by solid phase extraction (SPE) with a SDB-XC disk of 47 mm of diameter. The disk was rinsed with dichloromethane, and afterwards was conditioned with methanol and ultrapure water. After these steps, the sample was placed on the top of the disk, and by vacuum action it was drawn through it. The compounds NP, IGEPAL and OP were retained and then successive steps of drying and acetonitrile and acetone solvent recovery are carried out. The average recovery rate of extraction obtained by this process is 70%.

2.5.2. High-performance liquid chromatography

The equipment used was an Agilent 1100 Series HPLC chromatograph. The detector was a fluorescence detector (FLD) which $\lambda_{exciting}$ = 227 nm and $\lambda_{emission}$ = 316 nm. The concentration determinations were performed by injecting 80 μl of sample extract, into a column LiChroCART 250-4 of 5 μm and with an internal diameter of 4.6 mm the temperature was 25°C. The eluent used was a mixture of 80% acetonitrile with 20% water in an isocratic system with a flow rate of 0.8 ml/min.

3. Results and discussion

3.1. Sado river water characterization

Three samples of surface water from Sado River were collected. The samples were collected on May 18th 2009 (Monday), on June 18th 2009 (Thursday) and on October 14th 2009 (Wednesday). The characterization of these samples is presented in Table 1.

Table 1 data shows that the sample collected on Monday (May 18th) did not present EDs, while in the other two samples (collected during the week) EDs were detected.

3.2. Membrane characterization

The hydraulic permeability (L_p), the salts rejection coefficients, and the reference solute rejection coefficient of the NF 90, NF 200 and NF 270 membranes are presented in Table 2. L_p was determined at pressures between 10 and 30 bar. The salts and organic solute experiments were performed a 15 bar. All experiments were carried out at 25°C and at a feed circulation flowrate of 0.6 ml/min.

As it is shown in Table 2, the NF270 membrane has the highest hydraulic permeability and the lowest salt rejection coefficients.

Table 2
Membranes Characterization: hydraulic permeability (L_p), salt rejection coefficients to NaCl and Na_2SO_4 and rejection coefficient to Glucose. (25°C and a feed circulation flowrate of 0.6 ml/min)

	NF90	NF200	NF270
L_p (kg/h/m²/bar)	3.7	10.5	15.6
f NaCl (%)	97%	66%	48%
f Na_2SO_4 (%)	99%	98%	94%
f Glucose (%)	97%	90%	84%

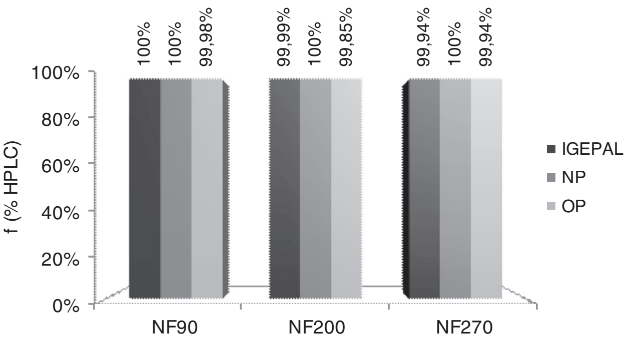

Fig. 3. Variation of rejection coefficients (f) to IGEPAL, NP and OP for membranes NF90, NF200 and NF270. Feed circulation flowrate: 0.6 l/min, operating pressure: 30 bar.

3.3. Permeation of NP, OP, IGEPAL model solutions

Permeation experiments with three NF membranes – NF 90, NF 200 and NF 270 – were carried out in order to evaluate the NF performance during the permeation of model solutions containing NP, OP and IGEPAL. The membranes NF90, NF200 and NF270 rejection coefficients to IGEPAL, NP and OP, presented in Fig. 3, are practically 100%.

3.4. Permeation of humic acid (HA) model solutions

Permeation experiments with HA model solutions were also carried out with the three membranes, NF90, NF200 and NF270.

Fig. 4 show the variation of the permeate fluxes with the transmembrane pressure in comparison with the hydraulic permeability of the membranes.

As it can be observed, the permeate fluxes obtained for the HA model solutions have a deviation from the linear behavior observed for water, being observed a limiting flux at 30 bar for the NF270 membrane. It is also observed that the fluxes are lower for the solutions that have higher ionic strengths (10^{-2} M). This behavior can be explained by the influence that the ionic strength has in the charge of the NOM colloidal solution [8].

Fig. 5 presents the average rejection coefficients to HA (determined in terms of TOC) obtained for different transmembrane pressures (10–35 bar) and for different ionic strengths (10^{-2} and 10^{-3} M). The apparent rejection coefficients to HA are independent of the transmembrane pressure and the values in Fig. 5 are average numbers obtained from for six transmembrane pressure values (10–35 bar).

It is also observed that for the NF90 membrane the HA rejection was about 100% for the solution with an ionic strength of 10^{-2} M, and 98% for the solution with an ionic strength of 10^{-3} M. For the NF200 membrane the rejections obtained were 100% and 95%, for the solutions

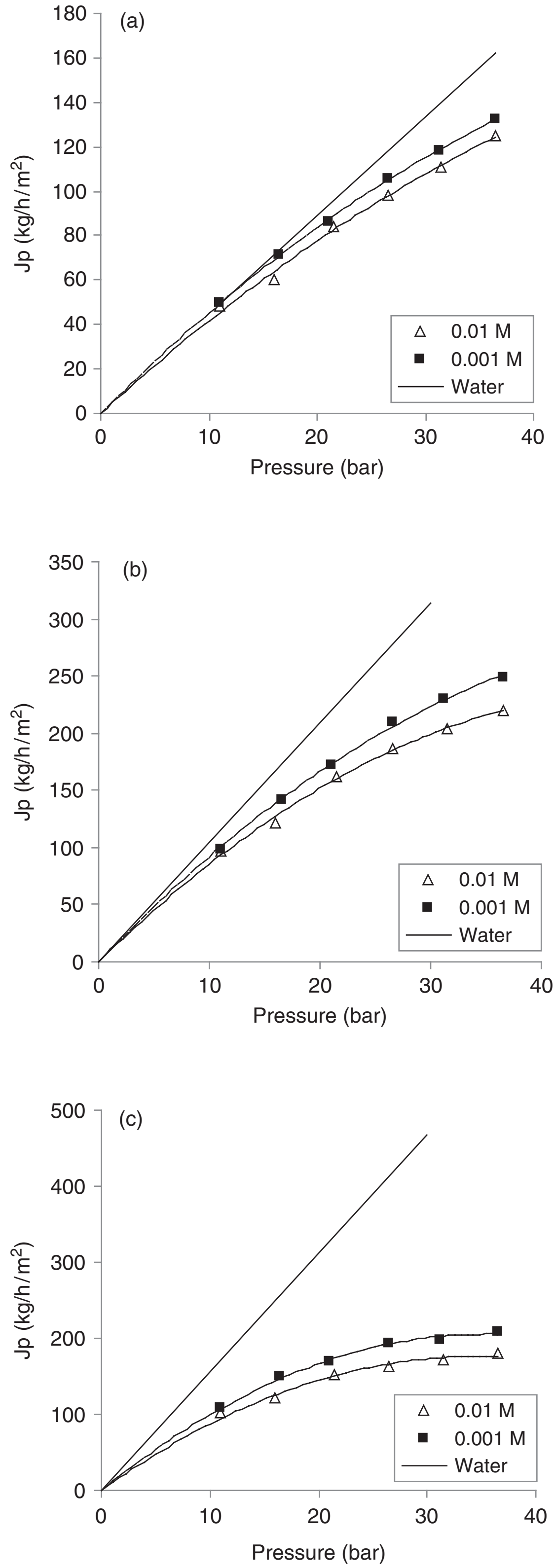

Fig. 4. Variation of permeation fluxes with pressure for the membranes NF90 (a), NF200 (b) and NF270 (c). Model solution of humic acid (10 mg/l) and ionic strengths of 10^{-2} M and 10^{-3} M. Feed circulation flowrate: 0.6 l/min, operating pressure: 10–35 bar.

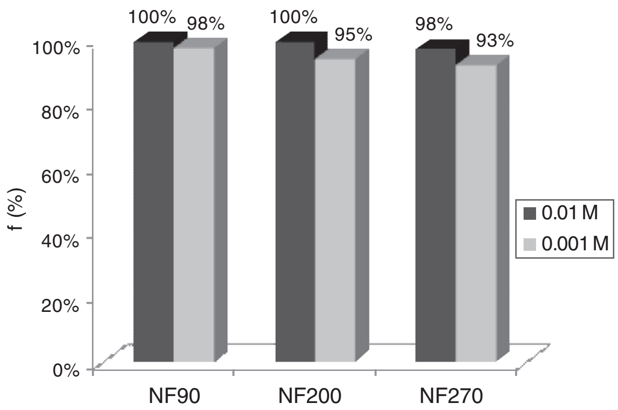

Fig. 5. Variation of humic acid average apparent rejection coefficients (*f*) with ionic strength (10^{-2} M and 10^{-3} M) for NF90, NF200 and NF270 membranes. Feed circulation flowrate: 0.6 l/min, operating pressure: 10–35 bar.

with ionic strengths of 10^{-2} M and 10^{-3} M, respectively. For the NF270 membrane the rejections obtained were 98% and 93%, for the solutions with ionic strengths of 10^{-2} M and 10^{-3} M, respectively. Therefore, it can be concluded that the decrease in the ionic strength leads to a decrease in the HA rejection.

3.5. Permeation of surface water (Sado river)

The experiments with the surface water were used to evaluate the permeate fluxes variation with water recovery rate (productivity) and to evaluate the NF permeates quality (in terms of NOM and ED) for the samples of Sado river, with and without inoculation of EDs. These results are presented in Figs. (6–9).

As it can be observed from Figs. (6–9) the permeate fluxes decrease with the increase of the WRR, being this

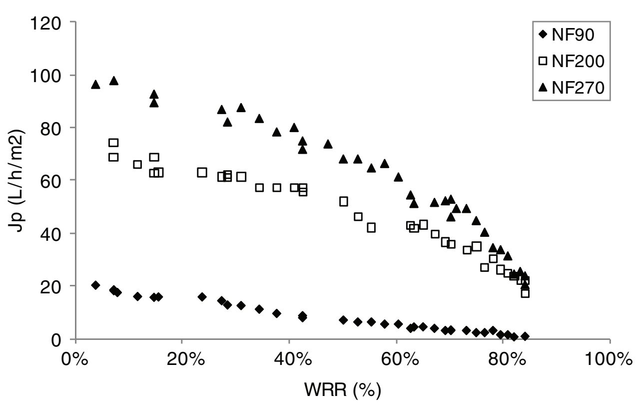

Fig. 6. Variation of NF90 (♦), NF200 (□) and NF270 (▲) permeate fluxes as a function of water recovery rate (WRR) for the raw sado river water. Transmembrane pressure: 30 bar and Temperature: 25°C (sample collected in June).

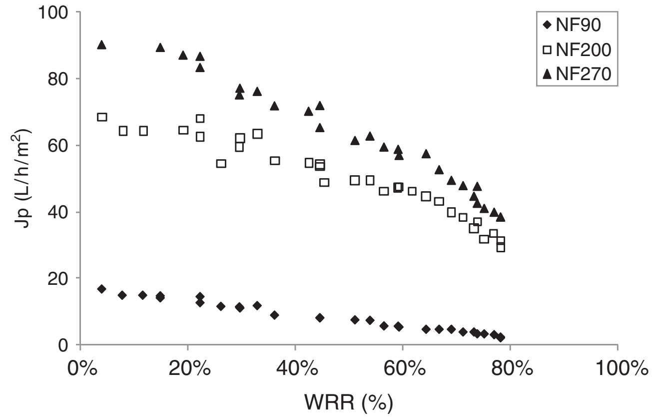

Fig. 7. Variation of NF90 (♦), NF200 (□) and NF270 (▲) permeate fluxes as a function of water recovery rate (WRR) for the EDs Inoculated Sado river water. Transmembrane pressure: 30 bar and Temperature: 25°C (sample collected in June).

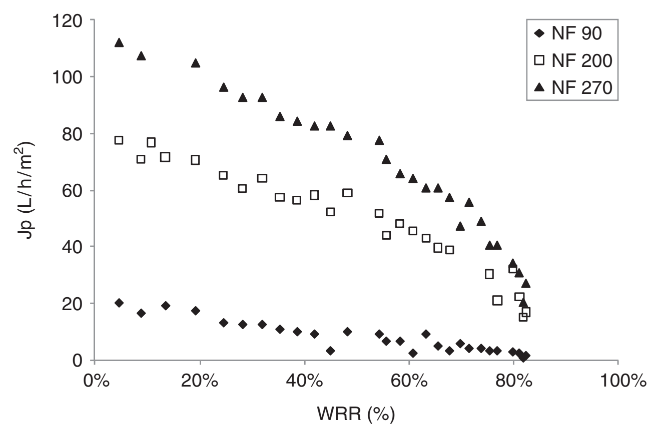

Fig. 8. Variation of NF90 (♦), NF200 (□) and NF270 (▲) permeate fluxes as a function of water recovery rate (WRR) for the raw sado river water. Transmembrane pressure: 30 bar and Temperature: 25°C (sample collected in October).

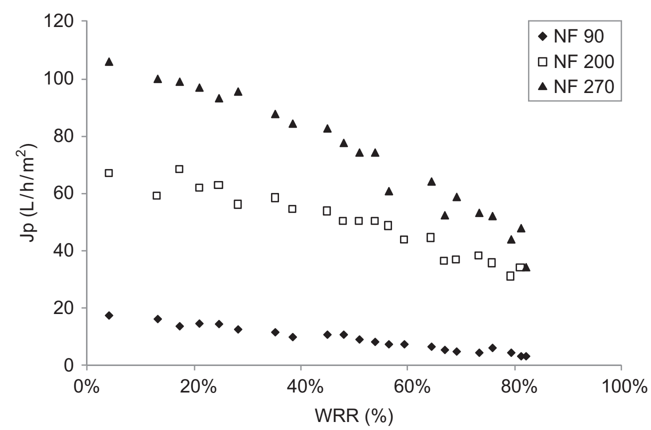

Fig. 9. Variation of NF90 (♦), NF200 (□) and NF270 (▲) permeate fluxes as a function of water recovery rate (WRR) for the Inoculated sado river water. Transmembrane pressure: 30 bar and Temperature: 25°C (sample collected in October).

decrease more pronounced towards the higher WRR. The NF 90 membrane is the one that has the lower fluxes, and the NF270 membrane presents the higher fluxes. The permeate flux decline, presented in Table 3, show that the flux decrease is less severe for the experiments with inoculation of EDs (Figs. 7 and 9) and this can be attributed to the fact that the natural organic matter interacts with the endocrine disruptors and leads to the minimization of the membrane fouling.

The removal of NOM was assessed through the quantification of the rejection coefficients calculated in terms of TOC. These results are presented in Table 4.

The apparent rejection coefficients obtained for NOM are independent of the WRR, for both inoculated and non-inoculated sado river water, and the NF90, NF200 and NF270 membranes present decreasing values, respectively. The average rejection coefficient for the NF90 membrane was 94%, for the NF200 membrane was 82% and for the NF270 membrane was 78%.

The feed and permeate content in terms of the EDs studied is presented in Tables 5 and 6.

The results presented in Tables 5 and 6 show that the EDs content in the permeates were below the detection level and therefore were totally rejected, for the surface water with and without inoculation and that for all membranes.

Table 3
Average flux decline of membranes NF90, NF200 and NF270 for the inoculated and non-inoculated sado river water. (WRR up to 80%, 30 bar, 25°C and a feed circulation flowrate of 0.6 ml/min)

Flux decline (%)		
ED Inoculation	No	Yes
NF90	95	81
NF200	75	50
NF270	82	65

Table 4
Average rejection coefficients to TOC of membranes NF90, NF200 and NF270 for the inoculated and non-inoculated sado river water. (30 bar, 25°C and a feed circulation flowrate of 0.6 ml/min)

Sample collection date	f_{NOM} (%)			
	June, 18th		October, 14th	
ED Inoculation	No	Yes	No	Yes
NF90	96	93	93	94
NF200	81	81	82	84
NF270	79	78	77	77

Table 5
Characterization of average feed and permeate streams in the raw sado river water – (sample collected in October 14th)

	Feed	Permeate		
		NF90	NF200	NF270
Conductivity$_{25°C}$ (mS/cm)	63.4	19.6	48.3	49.5
[IGEPAL] (μg/l)	0.001	n.d.	–	n.d.
[NP] (μg/l)	0.035	n.d.	n.d.	n.d.
[OP] (μg/l)	0.008	n.d.	n.d.	n.d.

n.d. – not detected.

Table 6
Characterization of average feed and permeate streams in the inoculated sado river water (sample collected in October 14th)

	Feed	Permeate		
		NF90	NF200	NF270
Conductivity$_{25°C}$ (mS/cm)	74.2	24.9	49.1	50.5
[IGEPAL] (μg/l)	1.682	n.d.	n.d.	n.d.
[NP] (μg/l)	12.271	n.d.	n.d.	n.d.
[OP] (μg/l)	12.271	n.d.	n.d.	n.d.

n.d. – not detected.

4. Conclusions

The rejection coefficients for model solutions of Nonylphenol Ethoxylate (IGEPAL), 4-Nonylphenol (NP) and 4-Octylphenol (OP) are approximately 100% for all the membranes – NF90, NF200 and NF270. These results support the idea that NF is a good method for the removal of these Endocrine Disruptors, since these compounds are totally rejected. The model solutions with 10 mg/l of humic acid, pH of 6.2 and an ionic strength of 10^{-2} M presented rejection coefficients of 100% for NF90 and NF200 membranes and of 98% for the NF270 membrane. For model solutions with 10 mg/l of NOM, with a pH of 6,2 and an ionic strength of 10^{-3} M the rejection coefficients were 98% for NF90, 95% for NF200 and 93% for NF270 membranes.

For the permeation experiments with the raw surface water, run in concentration mode, the permeate fluxes of membranes NF270 and NF200 decreased from 100 l/h/m^2 and 70 l/h/m^2, respectively, to final values of 20 l/h/m^2, at the recovery rate of 80%. For NF90 membrane the initial fluxes, 20 l/h/m^2, decreased till approximately zero for recovery rates of 80%. For the permeation experiments with the surface water inoculated with the endocrine disruptors the permeate fluxes of membranes NF270 and NF200 decreased from 100 $l/h/m^2$ and 70 $l/h/m^2$, respectively, to final values of 40 $l/h/m^2$, at the recovery rate of 80%. For NF90 membrane the initial fluxes, 20 $l/h/m^2$, decreased till approximately zero for recovery rates of 80%. The more permeable membranes, NF200 and NF270, presented lower flux declines in the case of the permeation of the surface water inoculated with the endocrine disruptors. This may be attributed to the fact that natural organic matter interacts with the endocrine disruptors and leads to the minimization of the membrane fouling.

The average apparent rejection coefficients obtained for NOM were 94% for the NF90 membrane, 82% for the NF200 membrane and 78% for the NF270 membrane. The rejection coefficients to endocrine disruptors, for all membranes were 100%, for the surface water with and without inoculation of endocrine disruptors. The higher rejection coefficients to endocrine disruptors when compared to the ones of natural organic matter give evidence that there is a NOM fraction of high molecular weight retaining the endocrine disruptors in the concentrate stream and a permeate stream with NOM of lower molecular weight that is free of endocrine disruptors.

References

[1] S. Hong and M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, J. Membr. Sci., 132 (1997) 159–181.

[2] J.W. Cho, G. Amy and J. Pellegrino, Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes, Water Res., 33(11) (1999) 2517–2526.

[3] Y. Kiso, Y. Sugiura, T. Kitao and K. Nishimura, Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes, J. Membr. Sci., 192(1–2) (2001) 1–10.

[4] Y. Kiso, A. Mizuno, R. Othman, Y.J. Jung, A. Kumano and A. Ariji, Rejection properties of pesticides with a hollow fiber NF membrane (HNF-1), Desalination, 143(2) (2002) 147–157.

[5] A.R. Costa and M.N. de Pinho, The role of membrane morphology on ultrafiltration for natural organic matter removal, Desalination, 145(1–3) (2002) 299–304.

[6] A.R. Costa and M.N. de Pinho, Coagulation/flocculation/ultrafiltration for natural organic matter removal in drinking water production, Water Sci. Technol. Water Supply, 4–5 (2004) 215–222.

[7] A.R. Costa and M.N. de Pinho, Performance and cost estimation of nanofiltration for surface water treatment in drinking water production, Desalination, 196(1–3) (2006) 55–65.

[8] A.R. Costa, M.N. de Pinho and M. Elimelech, Mechanisms of colloidal natural organic matter fouling in ultrafiltration, J. Membr. Sci., 281 (2006) 716–725.

[9] Y.J. Jung, Y. Kiso, H.J. Park, K. Nishioka and K.S. Min, Rejection properties of NF membranes for alkylphenols, Desalination, 202(1–3) (2007) 278–285.

[10] L.D. Nghiem, A.I. Schafer and M. Elimelech, Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms, Environ. Sci. Technol., 38 (2004) 1888–1896.

[11] A.I. Schafer, L.D. Nghiem and T.D. Waite, Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis, Environ. Sci. Technol., 37(1) (2003) 182–188.

[12] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Werta, and Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination, 202 (2006) 156–181.

[13] S. González, M. Petrovic and D. Barceló, Evaluation of two pilot scale membrane bioreactors for the elimination of selected surfactants from municipal wastewaters, J. Hydrol., 356(1–2) (2008) 46–55.

[14] M. Ahel, W. Giger and M. Koch, Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment-I: Occurrence and transformation in sewage treatment, Water Res., 28(5) (1994a) 1131–1142.

[15] M. Ahel, W. Giger and C. Schaffner, Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment 2. Occurrence and transformation in rivers, Water Res., 28(5) (1994b) 1143–1152.

[16] Official Journal of the European Communities, L 331, 15/12/2001, pp 5. (http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2001:331:0001:0005:EN:PDF).

[17] T. Isobe, H. Nishiyama, A. Nakashima and H. Takada, Distribution and Behavior of Nonylphenol, Octylphenol, and Nonylphenol Monoethoxylate in Tokyo Metropolitan Area: Their Association with Aquatic Particles and Sedimentary Distributions, Environ. Sci. Technol., 35(6) (2001) 1041–1049.

[18] R.A. Rudel, S.J. Melly, P.W. Geno, G. Sun and J.G. Brody, Identification of Alkylphenols and Other Estrogenic Phenolic Compounds in Wastewater, Septage, and Groundwater on Cape Cod, Massachusetts, Environ. Sci. Technol., 32(7) (1998) 861–869.

[19] D.T. Bennie, C.A. Sullivan, H.-B. Lee, T.E. Peart and R.J. Maguire, Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River, The Science of the Total Environment, 193(3) (1997) 263–275.

[20] M.A. Blackburn and M.J. Waldock, Concentrations of alkylphenols in rivers and estuaries in England and Wales, Water Res., 29(7) (1995) 1623–1629.

[21] A. Latorre, S. Lacorte and D. Barceló, Presence of Nonylphenol, Octyphenol and Bisphenol a in Two Aquifers Close to Agricultural, Industrial and Urban Areas, Chromatogr., 57(1–2) (2003) 111–116.

[22] D. Barceló, D. Azevedo, L. Silva and P. Viana, Occurrence of Nonylphenol and Bisphenol-A in Surface Waters from Portugal, J. Braz. Chem. Soc., 12(4) (2001) 532–537.

[23] M. Petrovic, A. Diaz, F. Ventura and D. Barceló, Simultaneous Determination of Halogenated Derivatives of Alkylphenol Ethoxylates and Their Metabolites in Sludges, River Sediments, and Surface, Drinking, and Wastewaters by Liquid Chromatography-Mass Spectrometry, Anal. Chem., 73(24) (2001) 5886–5895.

[24] M.J. López de Alda and D. Barceló, Determination of steroid sex hormones and related synthetic compounds considered as endocrine disrupters in water by fully automated on-line solid-phase extraction–liquid chromatography–diode array detection, J. Chromatogr. A, 911 (2001) 203–210.

[25] M.J. López de Alda and D. Barceló, Use of solid-phase extraction in various of its modalities for sample preparation in the determination of estrogens and progestogens in sediment and water, J. Chromatogr. A, 938(1–2) (2001) 145–153.

[26] A.R. Costa and M.N. de Pinho, Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions, J. Membr. Sci., 255(1–2) (2005) 49–56.

[27] M.D. Afonso and M.N. de Pinho, Ultrafiltration of bleach effluents in cellulose production, Desalination, 79(2–3) (1990) 115–124.