



Membrane filtration technologies applied to municipal secondary effluents for potential reuse

Juan L. Acero*, F. Javier Benitez, Ana I. Leal, Francisco J. Real, Fernando Teva

Departamento de Ingeniería Química y Química Física, Universidad de Extremadura, 06071 Badajoz, Spain

ARTICLE INFO

Article history:

Received 25 May 2009

Received in revised form 4 December 2009

Accepted 8 December 2009

Available online 16 December 2009

Keywords:

Ultrafiltration and nanofiltration membranes

Municipal secondary effluent

Permeate flux

Rejection coefficients

Removal of pharmaceuticals

ABSTRACT

Four UF membranes (denoted GH, GK, PT and PW with MWCO of 1000, 2000, 5000 and 20,000 Da, respectively) and four NF membranes (denoted DL, CK, DK and HL, with an approximate MWCO of 150–300 Da in all cases) were used for the filtration of an effluent generated in a municipal wastewater plant after a secondary treatment. The influence of the most important operating variables (nature and MWCO of the membranes, transmembrane pressure, tangential velocity, and temperature) on the permeate flux was widely discussed, and the resistances to the permeate flux were determined following the resistances in series model. Rejection coefficients for parameters that measure the global pollutant content of the effluent (chemical oxygen demand, total organic carbon, absorbance at 254 nm, turbidity, total nitrogen and total phosphorus) were also evaluated, and the results revealed that both UF and NF are feasible options for the treatment of this effluent, yielding a permeate stream that can be reused in several applications. Finally, 28 pharmaceutical compounds were initially detected in this effluent, and their respective rejection coefficients were determined, with eliminations higher than 75% in the case of NF with the HL membrane. Therefore, it is concluded that NF is an excellent option for the removal of toxic pharmaceuticals in municipal wastewaters.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The amount of effluents from municipal wastewater treatment plant (WWTP) has increased during the last decades, and due to more stringent EU regulations, the quality of WWTP effluents must be improved in the coming years. In addition, society's rapid evolution has increased the demand for higher quality water in every sector: industry, agriculture, urban consumption, etc. At the same time, the generation of substantial quantities of wastewaters has led to its consideration as an alternative water resource [1]. In effect, wastewater reuse has a major impact on sustainability: it reduces environmental damage and relieves the demand for natural freshwater sources [2]. Specifically, municipal wastewater can be reused to agriculture at all levels, urban and industrial uses, aquifer recharge, etc. However, advanced treatment (tertiary treatment) is required to minimize its potentially negative impact on public health [3], because more than 200 different chemical compounds – many of which may be acutely or chronically toxic to aquatic organisms and may pose a health risk to man and animals alike – have been identified in secondary effluents of municipal wastewater streams. Many of these chemicals (pharmaceuticals

and personal care products, endocrine disrupting compounds, etc.) are not easily degraded and may thus have long-term environmental effects [2].

According to this, optional tertiary treatment improves the quality of secondary wastewater and produces an effluent that can be used as a substitute of freshwater sources for household and industrial needs. Several physical–chemical processes have been investigated as tertiary treatment of secondary effluent, including ozone [4], photo-catalysis UV/TiO₂ [5], adsorption [2], as well as several sequences of different physical–chemical steps [6]. In recent years, membrane filtration becomes a novel technology in wastewater reclamation and reuse [7–11]. Compared with traditional physical–chemical treatment, membrane processes show irreplaceable advantages, such as low energy cost (mainly for pumping), low capital investment, chemicals requirements only for membrane cleaning, relative uncritical scale-up and high throughput while maintaining product purity under ambient conditions. The expected benefit of ultrafiltration (UF) and nanofiltration (NF) processes for WWTP effluent treatment lie in the quality and the very considerable improvement in disinfection of the permeate, making it suitable for unrestricted irrigation [1–2].

However, one of the major problems that membrane applications face is membrane fouling, defined as the drop in the membrane flux with time [12]. Fouling is due to several mechanisms such as adsorption of solutes onto the membrane, deposition

* Corresponding author. Tel.: +34 92 4289385; fax: +34 92 4289385.
E-mail address: jlacero@unex.es (J.L. Acero).

Table 1

Typical quality parameters of the selected secondary effluent.

COD (mg L ⁻¹)	49.7 ± 3.5
UVA ₂₅₄ (cm ⁻¹)	0.247 ± 0.014
TOC (mg L ⁻¹)	17.6 ± 1.9
Turbidity (NTU)	2.4 ± 0.3
pH	8.0 ± 0.2
Total nitrogen (mg L ⁻¹)	60.5 ± 5.5
Total phosphorus (mg L ⁻¹)	0.40 ± 0.03
Total solids (mg L ⁻¹)	400 ± 23
Suspended solids (mg L ⁻¹)	36 ± 9
Total coliforms (CFU/100 mL)	(1.0 ± 0.4) × 10 ⁶
Faecal coliforms (CFU/100 mL)	(1.3 ± 0.3) × 10 ⁵

of small colloidal particles on the membrane pores (pore blocking) and build up of particles in form of a cake layer [9]. Fouling due to pore blocking and cake formation is assumed to be the predominant mechanism in UF and NF membranes [13]. In general, fouling adds additional resistances to the flow, both external (cake layer) and internal (adsorption and pore blocking). In the operation of a membrane system, membrane fouling is dependent on many parameters such as membrane characteristics, feed water characteristics, and hydraulic conditions of the system.

Taking into account these considerations, in the present work, UF and NF batch concentration experiments (with recycling of the retentate stream) of secondary municipal wastewater were performed in order to clarify the fouling mechanisms and evaluate the retention of contaminants and the permeate quality. Thus, the specific objectives were: to study the evolution of the permeate flux with filtration time and volume retention factor; to establish the effect of operating parameters such as transmembrane pressure (TMP), tangential velocity (v), temperature (T) and nature and molecular weight cut-off (MWCO) of the membranes used on the permeate flux; to analyze the different resistances to the permeate flux to elucidate the fouling mechanisms; to determine the effectiveness of the filtration treatments by the evaluation of the rejection coefficients for several water quality parameters; and to assess the elimination of pharmaceutical compounds contained in the investigated effluent.

2. Materials and methods

2.1. Secondary municipal effluent

Secondary effluent samples used in this study were collected from a municipal wastewater treatment plant located in Mostoles (Madrid, Spain). This plant applies a pretreatment for solid removal, a primary sedimentation, an activated sludge biological treatment, and a final clarification. The water samples were stored at 4 °C until use. The main effluent quality parameters are presented in Table 1.

Table 2

Properties of target membranes (material, MWCO and salt rejection provided by manufacturer). PWP values were determined at 20 °C.

Membrane	Material	MWCO (Da)	pH	Contact angle (°)	PWP (L h ⁻¹ m ⁻² bar ⁻¹)	MgSO ₄ rejection (%)
PW	PES	20,000	2–11	61.3 ^a	100.4 ± 3.5	
PT	PES	5000	2–11	59.0 ^b	24.2 ± 0.8	
GK	TF	2000	2–11	<61	5.4 ± 0.3	
GH	TF	1000	2–11	<61	3.6 ± 0.1	
DL	TF	150–300	2–11	30.7 ^c	3.7 ± 0.1	96
CK	CA	150–300	2–8	59.0 ^b	2.7 ± 0.1	92 ^e
DK	TF	150–300	2–11	41.0 ^b	2.6 ± 0.1	98
HL	TF	150–300	3–9	41.0 ^d	8.4 ± 0.4	98

^a Ref. [15].^b Ref. [14].^c Ref. [16].^d Ref. [17].^e Measured as Na₂SO₄.

2.2. Equipment and experimental procedure

UF and NF experiments were carried out in the laboratory membrane equipment model P-28TM, supplied by CM-CELFA Membranentechnik AG (Seewen, Switzerland) that was described in detail in a previous publication [14]. This system operated in cross-flow mode (feed stream flowing tangentially to the membrane surface) and basically it was constituted by a 500 cm³ pressurized storage vessel and a gear pump which fed the solution into the device containing the membrane at the desired flow rates. The membranes had an effective area of 28 cm². The temperature of feed solution was maintained at the desired value by recirculation of water around the storage vessel throughout the experiment. The transmembrane pressure was controlled in every experiment performed by pressurizing the storage vessel with nitrogen, and the tangential velocity (v) was modified by changing the feeding flow rate with the gear pump. The experiments were performed at natural pH of the secondary effluent (around 8). A new membrane was used for each experiment, being previously soaked in ultrapure water for 24 h in order to eliminate preservative products.

The experiments were conducted in batch concentration mode; that is, with the permeate stream collected separately, and the retentate stream recycled to the feed tank. A standard protocol constituted by three steps was followed: in the first step, the new membrane was rinsed with ultrapure (UP) water, and the water permeate flux (J_w) was measured in order to determine the membrane hydraulic permeability (PWP). In the second step, the secondary effluent filtration process was performed: for this purpose, the storage tank was filled with the effluent (300 mL), and at regular time intervals, the cumulative permeate volume (V_p) was measured with a Mettler balance, which later provided the permeate flux (J_v). At the same time, samples of the feed, retentate and permeate streams were withdrawn in order to analyze the main water quality parameters. These experiments lasted until a volume reduction factor of 3 was reached, collecting around 200 and 100 mL of permeate and concentrate, respectively. In the third stage, once each secondary effluent filtration experiment was finished, the membrane was rinsed with ultrapure water in order to eliminate the cake layer. Then, the pure water permeate flux was measured again in order to determine the irreversible membrane fouling, and thus, the different resistances of the filtration process. The operating variables TMP, v and T , and the MWCO and nature of the membrane were modified in the different UF and NF experiments.

2.3. Membranes

The experiments were carried out by using different flat sheet commercial membranes provided by GE Osmonics (Florida, USA), with an effective surface area of 28 cm² in all cases. Concretely, four

UF membranes denoted GH, GK, PT, and PW with MWCOs of 1000, 2000, 5000, and 20,000 Da, respectively, were used. The main properties of these membranes are detailed in Table 2. The GK and GH membranes were made of thin film composite, with a cross-linked aromatic polyamide top layer, while the PT and PW membranes were of polyethersulfone. According to studies of these and similar membranes [15], polyamide membranes are less hydrophobic than polyethersulfone membranes. Although values of the contact angle for GK and GH membranes were not found in the literature, Park et al. [15] proposed a value of $44.7 \pm 1.2^\circ$ for the GM membrane, which is very similar to GK and GH. Therefore, the contact angle of GK and GH membranes must be lower than those of PW and PT membranes. All these membranes are negatively charged at neutral pH. The pure water permeability (PWP) was determined for each membrane by measuring the water permeate flux at different TMP. According to the values of PWP at 20°C summarized in Table 2, an increase in PWP was observed for UF membranes with higher MWCO as could be expected.

The four NF membranes also used (denoted DL, CK, DK, and HL; main properties also shown in Table 2) had similar MWCOs, in the range 150–300 Da according to the manufacturer. The DL, DK and HL membranes were made of thin film polyamide, and the CK membrane was of cellulose acetate. While the CK membrane is more hydrophobic, DL, DK and HL are more hydrophilic based on previously published data of contact angles [14,16–17]. All these membranes are also negatively charged at neutral pH. The different values of PWP experimentally obtained for these NF membranes with similar MWCO (Table 2) can be attributed to their internal structure, since this parameter is a characteristic inherently related to the composition, morphology, and hydrophobicity/hydrophilicity of the membranes. The highest PWP value was found for the HL membrane, similarly to the results obtained in previous investigations in which these membranes were used as well [18–19].

2.4. Analytical methods

All the analytical procedures were followed according to the Standard Methods [20]. Basically, the chemical oxygen demand (COD) was determined in a Dr Lange photometer (dichromate method); UV absorbance at 254 nm (UVA) was measured in a Unicam Helios β spectrometer; total organic carbon (TOC) was

analyzed in an IO Analytical total organic carbon analyzer, based on the persulfate oxidation method; turbidity was determined in a Hanna (HI93414) turbidity meter; total nitrogen (N) and total phosphorus (P) were determined by using Dr Lange cuvette-tests and photometer; total solids were determined by weighting an aliquot of the effluent after dryness; and suspended solid were obtained by filtering the sample through $0.45 \mu\text{m}$ filters. Finally, total and faecal coliforms assays were performed by using, respectively, m-Endo and m-FC culture media from Millipore, filtering 100 mL of water (containing $10 \mu\text{L}$ of secondary effluent or 1 mL of permeate) through $0.45 \mu\text{m}$ pore size membranes followed by incubation at the required temperature. The concentration of pharmaceutical compounds was analyzed by liquid chromatography–QTRAP–mass spectrometry (LC–QTRAP–MS/MS) after solid phase extraction (SPE) according to the method developed by Martinez-Bueno et al. [21].

3. Results and discussion

3.1. Permeate fluxes: influence of the operating conditions and determination of resistances

Filtration experiments of WWTP secondary effluent were performed with the selected UF and NF membranes, already described, by modifying the most important operating conditions: the nature and MWCO of the membranes, TMP, v and T (which is a characteristic of a secondary effluent). Table 3 summarizes the experiments performed with the specific values of these operating conditions. PT and HL membranes were mainly selected to investigate the influence of the operating variables because they provided the best results, as will be commented below.

The cumulative permeate volume (V_p) was obtained through each experiment and it did not increase linearly with processing time (data not shown), which is an indication of membrane fouling. Then, the permeate fluxes (J_v) were obtained from the V_p values by numerical differentiation of the collected mass vs time data. Thus, Fig. 1 represents the evolution of J_v with time for some selected UF (Fig. 1A) and NF (Fig. 1B) experiments. It can be observed that J_v decreased with the initial increase of time, specially in the experiments performed at higher TMP. Later, J_v decreased slightly until an almost constant value was reached at high processing time, depending that time on the experimental conditions. As it has been reported [22], the decline in J_v is a consequence of the several causes of membrane fouling, such as cake layer formation, pore blocking, or the adsorption of solutes onto the membranes. According to the profiles of J_v , membrane fouling occurred predominantly at the initial processing times. The main reason for this decline in flux is probably the initial fast pore blocking and adsorption of hydrophobic organic matter onto the membrane surface and into the membrane pores, followed by the formation of the cake layer [23]. Similar trends could be deduced for the evolution of J_v with volume reduction factor (VRF). This factor is an important parameter in batch concentration operating mode, and is defined as the ratio between the initial feed volume V_0 and the volume of the resulting retentate V_R , i.e., the volume remaining in the storage vessel ($V_R = V_0 - V_p$) [24]:

$$\text{VRF} = \frac{V_0}{V_R} \quad (1)$$

The permeate flux decreased with VRF as well as the filtration time did. The experiments conducted lasted until $\text{VRF} = 3$, and the predominant flux decline occurred from $\text{VRF} = 1$ to $\text{VRF} = 2$. The values of J_v determined at the end of each experiment ($\text{VRF} = 3$) are presented in Table 3, as well as the ratio secondary effluent/pure water permeates (J_v/J_w), which was also calculated for all the experiments at $\text{VRF} = 3$. This ratio J_v/J_w is an indirect measurement of the

Table 3

Experimental conditions applied in the filtration experiments performed and permeate fluxes and flux reduction obtained at $\text{VRF} = 3$.

Expt.	Membrane	TMP (bar)	v (m s^{-1})	T ($^\circ\text{C}$)	J_v ($\text{L h}^{-1} \text{m}^{-2}$)	J_v/J_w
UF1	PW	4	2	20	133.2	0.33
UF2	PW	6	2	20	160.4	0.27
UF3	PT	4	2	20	75.7	0.76
UF4	PT	6	2	20	103.2	0.71
UF5	PT	9	2	20	142.6	0.65
UF6	PT	6	1	20	78.1	0.55
UF7	PT	6	0.5	20	68.9	0.46
UF8	PT	6	2	10	80.0	0.72
UF9	GK	9	2	20	37.2	0.74
UF10	GH	9	2	20	24.1	0.75
NF1	DL	20	2	20	60.9	0.83
NF2	DL	30	2	20	92.1	0.82
NF3	CK	30	2	20	58.2	0.72
NF4	DK	30	2	20	61.1	0.79
NF5	HL	10	2	20	69.2	0.82
NF6	HL	20	2	20	135.2	0.78
NF7	HL	30	2	20	190.0	0.75
NF8	HL	30	1	20	162.9	0.61
NF9	HL	30	0.5	20	127.2	0.46
NF10	HL	30	2	10	160.2	0.80
NF11	HL	30	2	30	242.6	0.71

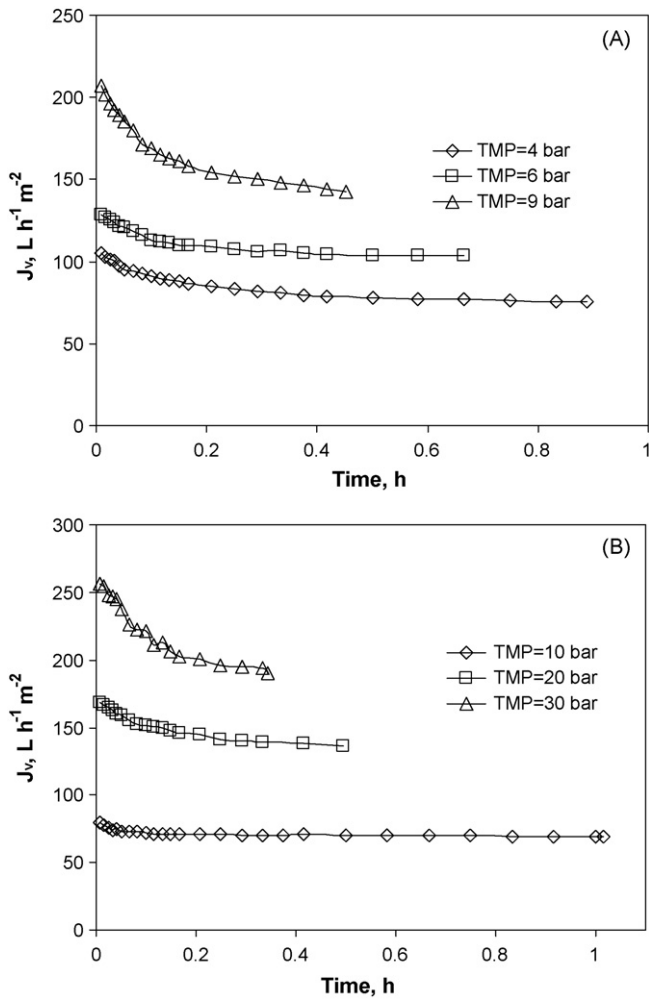


Fig. 1. Effect of TMP on the evolution of the permeate flux with processing time for the secondary effluent filtration experiments performed with (A) PT and (B) HL membranes. Experimental conditions: $v = 2 \text{ m s}^{-1}$ and $T = 20^\circ\text{C}$ (Expts. UF3–UF5 and NF5–NF7 in Table 3).

permeate flux decline, being the flux decline higher when the ratio J_v/J_w is lower. In general, flux decline was higher in UF experiments, which means that the UF membranes were more prone to fouling than NF membranes. As it has been reported, very high-molecular weight organic material comprised of hydrophilic components, such as soluble microbial products and extracellular polymeric substances, are the major cause of membrane fouling during the UF of secondary effluents [11,25].

From the values depicted in Table 3, it can be deduced that J_v is affected by the main operating parameters: TMP, MWCO and nature of the membranes, v , and T . Specifically for the influence of TMP, Fig. 2 represents the J_v values obtained vs TMP for two selected UF membranes (PW and PT, Fig. 2A) and two selected NF membranes (DL and HL, Fig. 2B). As can be observed, the permeate flux increased with the increase in the applied TMP, typical behaviour found in membrane processes [26–27]. Additionally, a nonlinear variation of J_v with TMP can be deduced, with smaller increases of J_v at high TMP. Thus, the relative difference between J_w and J_v became greater at high TMP, leading to a higher permeate flux decline, and therefore to a lower J_v/J_w ratio. This membrane fouling at high TMP was more pronounced in membranes with higher MWCO (UF membranes), being specially significant for the PW membrane with MWCO of 20 kDa (Fig. 2A). Similar greater membrane fouling at high TMP was observed in the filtration of cork processing wastewater

using membranes with MWCO > 40 kDa [28]. On the contrary, the increase of J_v with TMP was almost linear in the experiments performed with the NF membranes (Fig. 2B) due to the lower fouling of these membranes.

With respect to the influence of MWCO on J_v , the comparison of J_v values obtained in experiments performed under similar experimental conditions with different UF membranes leads to the following sequence $\text{PW} > \text{PT} > \text{GK} > \text{GH}$. Thus, for a given TMP value, an increase of the permeate flux with increasing MWCO was observed. In effect, a membrane with lower MWCO exerts increasing resistance to the pass of the solution. In addition, a greater flux decline was observed in the UF membranes with higher MWCOs. Thus, the flux decline with respect to the pure water flux at TMP of 9 bar was around 25, 26 and 35% for membranes GH, GK, and PT with MWCOs of 1, 2 and 5 kDa, respectively; and around 70% for the PW membrane with MWCO of 20 kDa (from the results obtained at 4 and 6 bar). However, in the NF process no conclusion could be drawn about the effect of the MWCO, as the four membranes presented similar pore sizes (in the range 150–300 Da). At the same time, Fig. 3 shows that, for a given TMP of 30 bar, the HL membrane provided the highest permeate flux, intermediate value when using the DL membrane, and the lowest values with the DK and CK

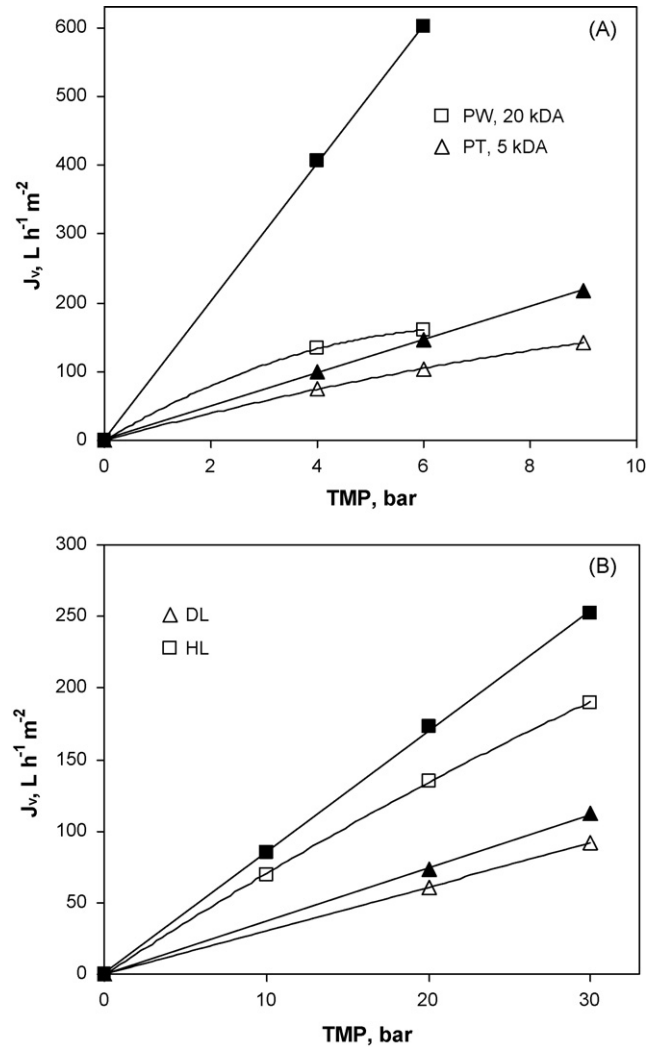


Fig. 2. Effect of TMP on the permeate flux obtained at VRF = 3 in (A) UF experiments performed with PW and PT membranes and (B) NF experiments carried out with DL and HL membranes. Full symbols correspond to pure water permeate flux (J_w) and open symbols correspond to secondary effluent permeate flux (J_v). Experimental conditions detailed in Table 3.

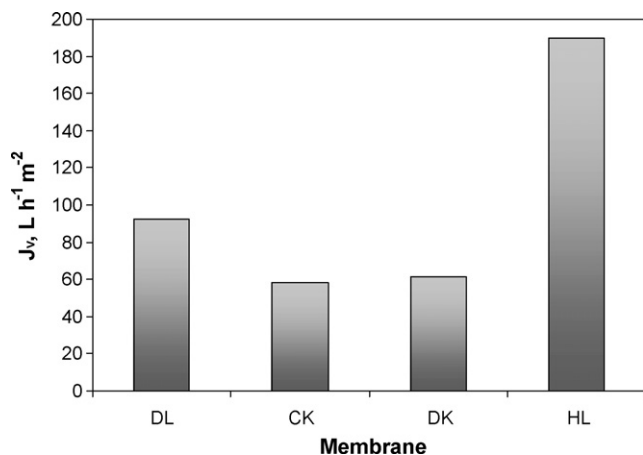


Fig. 3. Influence of the nature of the NF membranes on the permeate flux obtained at VRF = 3. Experimental conditions: TMP = 30 bar, $v = 2 \text{ m s}^{-1}$ and $T = 20^\circ\text{C}$.

membranes. As this trend agrees with the values of PWP presented in Table 2, the differences can be attributed to the different nature of the membranes. In effect, the NF of ultrapure water also gave the highest permeability for the HL membrane, intermediate for the DL membrane, and the lowest for the CK and DK membranes. Nevertheless, the highest flux decline (28%) with respect to the ultrapure water flux was obtained for the CK membrane, which can be attributed to its hydrophobic character, which promotes adsorption of organic compounds and leads to a decrease of the effective pore size and a consequent decrease of the water flux.

The effect of the tangential velocity on the permeate flux can be deduced from the values of J_v detailed in Table 3, that were obtained in those experiments in which this variable was modified (UF4, UF6 and UF7; and NF7, NF8 and NF9). As can be observed, J_v increased significantly when the tangential velocity was increased, probably due to a rise of the turbulence at the membrane interface, which removed some of the accumulated components in the cake layer by hydrodynamical forces, and thus reducing the cake and polarization layers [22]. As a consequence, the flux decline was lower in the experiments performed with higher tangential velocity, leading to higher values of the ratio J_v/J_w . This positive influence of v on J_v was observed for both UF and NF processes, indicating that external fouling must contribute significantly to the overall fouling phenomenon. Similarly, in the UF of some industrial wastewaters,

with higher organic contents, clear increases in the permeate flux with increasing cross-flow velocity were reported [29–30].

Finally, J_v increased with the increase of temperature from 10 to 20 °C in UF experiments performed with the PT membrane (Expts. UF8 and UF4) and from 10 to 30 °C in NF experiments carried out with the HL membrane (Expts. NF10, NF7 and NF11). At the same time, higher permeate flux decline was observed at higher temperature, specially in the NF experiments, decreasing the ratio J_v/J_w from 0.80 at 10 °C to 0.71 at 30 °C. These results can be explained by a higher diffusivity of organics in the water and by a greater gelatinization of polymeric substances at the membrane surface at higher temperatures [14].

In general, the decline of the permeate flux in a filtration process can be explained by means of the resistances in series model. As was previously described [14], when a wastewater is being filtrated, the permeate flux is represented by the general Darcy's law:

$$J_v = \frac{\text{TMP}}{\mu R_t} \quad (2)$$

where J_v represents the permeate flux of the wastewater, R_t corresponds to the total hydraulic resistance, and μ is the viscosity of the wastewater. In the case of filtration of pure water, a similar equation can be used with the terms J_w (permeate flux of pure water) and R_m (hydraulic resistance of clean membrane) instead of J_v and R_t , which allows the calculation of R_m :

$$J_w = \frac{\text{TMP}}{\mu R_m} \quad (3)$$

The total resistance is the result of several resistances in series:

$$R_t = R_m + R_f = R_m + R_{ef} + R_{if} \quad (4)$$

where R_m was previously commented; and R_f is the fouling resistance, which at the same time is the sum of the external (R_{ef}) plus the internal (R_{if}) fouling resistances. R_{ef} is mainly due to deposition of a cake layer on the membrane surface, and therefore, it can be removed by cleaning with UP water after the filtration experiment of the secondary effluent, as was described in Section 2. On the contrary, R_{if} is due to pore blocking and adsorption of materials onto the membrane surface and pores, which cannot be removed by water cleaning [10].

The described resistances were determined from permeate flux data obtained in the filtration experiments and by using Eqs. (2)–(4): R_m from filtration of pure water with the new membrane

Table 4
Resistances obtained in the filtration of secondary effluents at VRF = 3.

Expt.	$R_m \times 10^{-13} \text{ (m}^{-1}\text{)}$	$R_t \times 10^{-13} \text{ (m}^{-1}\text{)}$	$R_f \times 10^{-13} \text{ (m}^{-1}\text{)}$	$R_{if} \times 10^{-13} \text{ (m}^{-1}\text{)}$	$R_{ef} \times 10^{-13} \text{ (m}^{-1}\text{)}$	$(R_f/R_t) \times 100 \text{ (\%)}$
UF1	0.35	1.08	0.73	0.29	0.43	67.2
UF2	0.36	1.35	0.99	0.41	0.57	73.3
UF3	1.44	1.90	0.46	0.28	0.18	24.3
UF4	1.48	2.09	0.61	0.27	0.34	29.1
UF5	1.49	2.27	0.78	0.29	0.49	34.5
UF6	1.52	2.76	1.25	0.45	0.80	45.1
UF7	1.44	3.14	1.70	0.50	1.20	54.1
UF8	1.94	2.70	0.76	0.32	0.43	28.0
UF9	6.70	8.70	2.01	1.03	0.98	23.0
UF10	10.10	13.44	3.34	1.50	1.84	24.8
NF1	9.83	11.82	1.98	0.02	1.96	16.8
NF2	9.60	11.73	2.13	0.01	2.12	18.1
NF3	13.43	18.56	5.13	0.99	4.13	27.6
NF4	14.04	17.68	3.64	0.09	3.55	20.6
NF5	4.24	5.20	0.96	0.23	0.73	18.4
NF6	4.16	5.33	1.16	0.24	0.92	21.8
NF7	4.29	5.68	1.39	0.30	1.09	24.5
NF8	4.03	6.63	2.60	0.17	2.43	39.2
NF9	3.94	8.49	4.55	0.36	4.19	53.5
NF10	5.40	6.74	1.34	0.23	1.11	19.9
NF11	3.18	4.45	1.27	0.16	1.11	28.5

and prior to the filtration of the secondary effluent; R_t from the filtration of the secondary effluent in every experiment performed; and the combination $R_m + R_{if}$ from the second pure water filtration step, after finishing the experiment and cleaning the membrane with pure water. Finally, R_f and R_{ef} were calculated according to Eq. (4), by using the determined values of R_m , R_t and R_{if} . Following this procedure, Table 4 summarizes the different resistances obtained in every experiment conducted. It can be noted that, in general terms, the contribution to the total resistance of the fouling resistance (combined external plus internal) was lower than the inherent resistance of the clean membrane, excepting Expts. UF1 and UF2 carried out with the PW membrane, and Expts. UF7 and NF9 performed with $v = 0.5 \text{ m s}^{-1}$, which show an important fouling phenomenon ($R_f/R_t \times 100 > 50\%$).

Specifically in the UF process, at the same operating conditions R_f increased for membranes with lower MWCO (sequence $PW < PT < GK < GH$), as well as R_m did. However, the contribution of R_f to the total resistance was more significant in the membranes with higher MWCO (PW and PT). Thus, for the PW membrane (MWCO of 20 kDa), R_f contributed to around 70% of R_t , and R_m provided the remaining 30%. In the case of the GK and GH membranes (MWCO of 2 and 1 kDa, respectively), the contribution of R_f to the total resistance was only about 24%. Therefore, the fouling resistance was more important than the inherent membrane resistance only in those membranes with high MWCO. In addition, the values of R_{if} and R_{ef} obtained in each experiment are comparable, or at least of the same order of magnitude. As a result, the contribution of both external fouling (mainly due to cake formation) and internal fouling (due to pore blocking and adsorption) were similar in the selected UF membranes.

In the case of NF membranes, all of them with similar MWCO, R_m was more important than R_f for all the membranes tested; that is ($R_f/R_t \times 100 < 50\%$), except for the mentioned experiment NF9. The fouling resistance in the different membranes (TMP=30 bar, $v = 2 \text{ m s}^{-1}$ and $T = 20^\circ\text{C}$) followed the sequence $HL < DL < DK < CK$. The highest value of R_f corresponding to the CK membrane can be explained by its hydrophobic character. Effectively, the internal fouling was only significant for the CK membrane, which is a consequence of the higher amount of organic matter adsorbed on this membrane. Nevertheless, the external component of the fouling resistance was much higher than the internal component (unrecoverable by physical cleaning) for the selected NF membranes: it indicates that the cake layer provided a higher contribution than the adsorbed particles which remained inside the membrane after the washing stage with pure water. Cake layer filtration would be predominant when particles are larger than the pore size, as it occurs in NF, while pore blocking would be caused by components dimensionally comparable with the pore size. Similar low internal fouling was obtained by Manttari et al. [31] during the NF of effluents from the pulp and paper industry with the NF270 membrane.

With respect to the influence of TMP, it can be observed in Table 4 that R_t increased with TMP in both processes, UF and NF, which is due to the increment of fouling with TMP. Actually, for the UF PT membrane, an increase of TMP led to an increase of R_f from 0.46×10^{13} to $0.78 \times 10^{13} \text{ m}^{-1}$, which is mainly due to the rise of the external fouling, being the internal fouling fairly constant (Expts. UF3–UF5). Similarly, in the case of the NF HL membrane, R_f increased from TMP = 10 bar to 30 bar (see Expts. NF5–NF7) mainly due to the increase of R_{ef} , because R_{if} remained almost constant. As a result, higher TMP led to higher contributions of the fouling resistance to the total resistance (24.3–34.5% and 18.4–24.5% for the PT and HL membranes respectively), which resulted in an increase of the flux reduction with TMP as commented above. This increment of fouling, specially its external contribution, can be explained by the greater compression of the cake layer at high TMP.

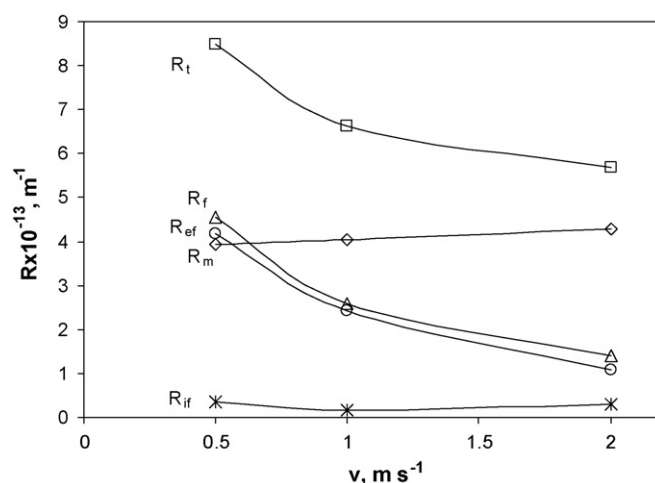


Fig. 4. Influence of the tangential velocity on the different resistances determined in the NF experiments performed with the HL membrane at 20°C and $\text{TMP} = 30 \text{ bar}$.

Fig. 4 shows the influence of the tangential velocity on the resistances for the HL membrane at $\text{TMP} = 30 \text{ bars}$ and 20°C (Expts. NF7–NF9). The membrane resistance R_m remained almost constant at different tangential velocities, as could be expected. A similar behaviour can be observed for R_{if} . However, R_{ef} decreased with the increase in the tangential velocity, because an increase in this velocity reduced the accumulation of solutes on the membrane surface (cake layer). Similar tendencies were obtained for the experiments performed with the UF PT membrane. Consequently, the decrease of R_{ef} with R_{if} and R_m almost constants led to decreases of R_t and R_f .

Finally, the influence of the temperature on the resistances was investigated in experiments performed with the PT membrane (Expts. UF8 and UF4 at 10 and 20°C) and with the HL membrane (Expts. NF10, NF7 and NF 11 at 10 , 20 and 30°C). It is obtained that R_m decreased with increasing temperature, due to lower values of the viscosity of the liquid. On the contrary, R_f decreased slightly with temperature in the UF experiments, indicating a slightly less severe fouling phenomena at higher temperature, while remained almost constant in the NF experiments. Similarly, R_{if} and R_{ef} decreased slightly with temperature in the UF experiments. As a consequence, a temperature increase resulted in a similar contribution of the fouling resistance to the total resistance in the UF experiments. However, the contribution of the fouling resistance increased at higher temperature in the NF experiments from 19.9% at 10°C to 28.5% at 30°C .

In conclusion, and according to the values of permeate flux and flux reduction summarized in Table 3 and the values of the different resistances detailed in Table 4, it is demonstrated that the membranes PT and HL provided the best results among the selected UF and NF membranes, because both presented good permeate flux with relatively low fouling phenomena. Under similar experimental conditions, the PT membrane (MWCO of 5 kDa) provided almost the same permeate flux than the PW membrane (MWCO of 20 kDa), and much higher than GK and GH membranes (MWCO of 2 and 1 kDa, respectively). On the other hand, although the different NF membranes tested had similar MWCO, the HL membrane provided the highest permeate flux.

3.2. Rejection coefficients for several water quality parameters

The effectiveness of the filtration processes in the removal of the organic matter present in this municipal secondary effluent was evaluated by the rejection coefficients, which were referred to several water quality parameters or pollution indices. As was

Table 5

Rejection coefficients (expressed as rejection percentages) obtained for several water quality parameters in the filtration of secondary effluents (VRF = 3).

Expt.	f_{COD} (%)	f_{TOC} (%)	f_{UVA} (%)	f_{turb} (%)	f_{N} (%)	f_{P} (%)
UF1	59.3	56.6	59.8	78.9	23.9	56.2
UF2	60.3	58.2	62.6	82.6	25.8	61.2
UF3	57.7	57.9	65.3	83.3	23.9	60.1
UF4	64.0	58.0	65.8	86.0	30.9	58.9
UF5	60.7	56.3	68.9	88.6	34.2	62.9
UF6	57.5	53.2	65.4	89.3	22.2	58.7
UF7	52.7	48.2	56.0	84.2	14.7	57.3
UF8	66.5	59.1	70.4	85.4	36.0	62.8
UF9	67.3	59.5	72.5	81.5	26.7	61.8
UF10	68.6	65.8	74.0	83.9	26.0	61.8
NF1	89.4	87.4	91.3	82.7	57.0	84.6
NF2	93.0	90.2	94.0	89.7	53.4	94.7
NF3	84.5	83.0	87.0	80.4	70.2	89.4
NF4	89.6	85.7	95.2	85.7	63.9	97.0
NF5	88.4	84.4	95.5	83.3	54.0	94.2
NF6	91.5	89.6	95.8	85.7	58.5	95.6
NF7	93.7	89.6	95.8	85.4	59.0	98.3
NF8	89.6	85.5	94.9	85.4	45.3	96.5
NF9	88.8	83.2	91.3	83.6	45.0	95.7
NF10	93.9	87.9	97.0	85.7	65.8	89.9
NF11	92.9	84.7	95.3	81.7	48.6	93.4

previously explained, the water quality parameters selected in the present work were: chemical oxygen demand (COD), total organic carbon (TOC), absorbance at 254 nm (UVA), turbidity (turb), total nitrogen (N) and total phosphorus (P). The rejection coefficient for the specific case of COD was defined by:

$$f_{\text{COD}} = \frac{\text{COD}_F - \text{COD}_P}{\text{COD}_F} \quad (5)$$

where COD_F and COD_P represent the COD in the feed and permeate streams respectively. Similar equations were used for the remaining rejection coefficients (f_{TOC} for TOC, f_{UVA} for UV absorbance at 254 nm, f_{turb} for turbidity, f_{N} for total nitrogen, and f_{P} for total phosphorus content). These rejection coefficients were determined at different filtration time in the experiments performed. In general, the retention of the main water quality parameters decreased slightly with the filtration time, due to the gradual increase of the concentration gradient, and also, to the decrease in the adsorption rate during the experiments because of the saturation of the membrane. The values obtained for the rejection coefficients at the end of the experiments (VRF = 3) are summarized in Table 5.

The observation of the values depicted in Table 5 allows the deduction of several general trends with respect to the influence of the modified operating variables. Firstly, the rejection coefficients sequence achieved was slightly different for UF or NF membranes: thus, turbidity > absorbance at 254 nm > COD > TOC \approx phosphorus \gg nitrogen for UF; and absorbance at 254 nm > phosphorus \approx COD > TOC > turbidity > nitrogen for NF. On the other hand, lower removals of these water quality parameters were obtained in the UF process: higher than 80% for turbidity, in the range 60–80% for absorbance at 254 nm, phosphorus, COD and TOC and lower than 36% for nitrogen. On the contrary, higher removals were obtained in the NF process, as could be expected for membranes with much lower MWCO: more than 80% for all the selected parameters, excepting nitrogen. In conclusion, these filtration processes led to moderate (UF) and high (NF) elimination of the organic matter content present in the secondary effluent. Regarding to the removal of total phosphorus, it was also moderate (UF) or high (NF), which could be explained if the phosphorus is present in organic compounds, forming complexes with high molecular weight; or as polyphosphates or phosphates, which are repelled by negatively charged membranes like those used in the present work [31]. On the contrary, the elimination of total nitrogen was rather limited in NF and low in

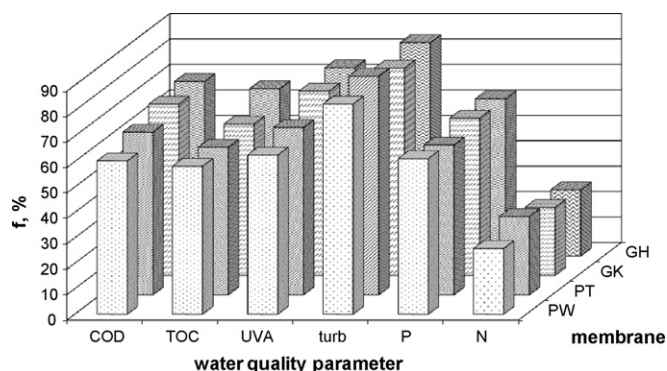


Fig. 5. Influence of the MWCO and nature of the selected UF membranes on the rejection of water quality parameters at VRF = 3 (Expts. UF2, UF5, UF9 and UF10 in Table 3).

UF, probably because of the low retention of nitrogen-containing organic compounds. Only nitrogen present as nitrite and nitrate anions would be partially repelled by negatively charged membranes. Furthermore, high molecular mass substances contained in a municipal secondary effluent might adsorb ions and improve their retention. With respect to the elimination of microorganisms, both total and faecal coliforms were not identified in the permeate of any experiment; and thus, a total removal of coliforms was achieved with UF and NF membranes. Lonigro et al. [3] also observed completely removal of Giardia cyst and Cryptosporidium oocyst in UF of municipal wastewater. Therefore, membrane filtration is useful for removal of potentially pathogenic coliforms or protozoan cyst from wastewater to be reused.

Secondly, there are slight influences of the operating variables (TMP and v) on these rejection coefficients. Thus, from the results summarized in Table 5, it can be only observed a slight positive influence of v on the rejection coefficients, which is due to the accumulation of solutes at higher tangential velocities (Expts. UF7, UF6 and UF4; and NF9, NF8 and NF7). However, the MWCO of the UF membranes presented a clearer influence on the parameters reflecting the removal of organic matter (COD, TOC and UVA), as can be seen in Fig. 5, which shows the f values for experiments performed with the four membranes tested under similar experimental conditions (Expts. UF2, UF4, UF9 and UF10). Thus, the rejection coefficients followed the sequence GH > GK > PT > PW with MWCO of 1, 2, 5 and 20 kDa respectively. On the contrary, the different MWCO of these membranes did not exert an apparent influence on the removal of turbidity, total phosphorus and total nitrogen. In a similar way, Fig. 6 represents the rejection coefficients obtained with the selected NF membranes (Expts. NF2–NF4 and NF7). It can be observed that the f values for COD, TOC, UVA, T and P were similar for the membranes DL, DK and HL, and lower for the mem-

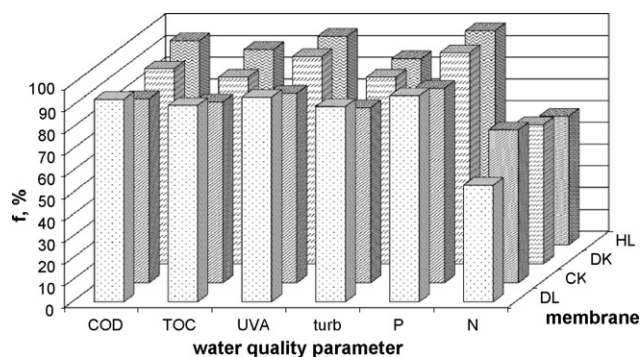


Fig. 6. Influence of the nature of the selected NF membranes on the rejection of water quality parameters at VRF = 3 (Expts. NF2, NF3, NF4 and NF7 in Table 3).

brane CK. On the contrary, the removal of total nitrogen followed the sequence CK > DK > HL > DL. One could expect higher rejection of organic matter with the more hydrophobic CK membrane, due to the higher capacity to adsorb hydrophobic organic compounds. Instead, the lower values of rejection coefficients in this CK membrane could be explained by the low contribution of adsorption to the overall removal of organic compounds and by its higher pore size.

As it has been reported, there are several factors affecting retention of pollutants and their retention mechanisms [32–33]. The main key solute parameters that primarily affect solute retention are molecular weight (MW), molecular size (length and width), acid dissociation constant (pK_a), hydrophobicity/hydrophilicity ($\log K_{ow}$) and polarity (dipole moment). Similarly, key membrane properties affecting retention are MWCO, pore size, surface charge and hydrophobicity/hydrophilicity. In general, the dominant mechanism for retention of organic matter would be size exclusion. In effect, the permeation through membranes will be easier for small molecules than for larger molecules, and the retention will generally increase with molecular size. As a consequence, the rejection factors of the selected water quality parameters would be higher in the NF membranes with lower MWCO, as it occurs in this work (see Table 5). However, other retention mechanisms such as adsorption and pore blocking are also important in membranes with MWCO higher than the molecular weight of the solutes, which typically occurs in the UF process. Both, pore blocking and adsorption, may narrow the membrane pores and lead to higher rejections [33]. In addition, electrostatic repulsion must also occur between negatively charged membranes and solutes with negative charge, such as anions and deprotonated organic moieties. Furthermore, fouling and rejection mechanisms of secondary municipal wastewater isolates on UF and NF membranes were investigated by Jarusuthirak et al. [34]. Thus, while the colloid fraction fouled UF and NF membranes primarily due to the effects of pore blockage, the hydrophobic and transphilic fractions were rejected by electrostatic repulsion.

According to these previous considerations and to the values of R_{if} and R_{ef} discussed above, adsorption and pore blocking must contribute to the retention of solutes predominantly in the UF membranes and in the case of the hydrophobic NF CK membrane. Other retention mechanisms, such as size exclusion, electrostatic repulsion and adsorption on the cake layer, must therefore participate in the retention of solutes, specially in the case of hydrophilic NF membranes.

In addition to the good permeate flux and relatively low fouling phenomena occurring in this system, the membranes PT and HL provided excellent results, among UF and NF membranes respectively, for the retention of solutes. Thus, the values of some water quality parameters in the permeate stream generated in the UF and NF processes were, respectively, 15–23 and 3–7 mg L^{-1} for COD, 0.06–0.10 and 0.01–0.03 cm^{-1} for UV absorbance at 254 nm, 5–8 and 2–3 mg L^{-1} for TOC and 0.3–0.5 and 0.3–0.4 NTU for turbidity. Therefore, these membranes are feasible options for the treatment of secondary effluent from municipal wastewater, with the goal to obtain a permeate with good physico-chemical and microbiological quality, which can be reused in several applications such as irrigation, aquifer recharge, etc.

3.3. Rejection of pharmaceutical compounds present in the secondary effluent

The initial concentrations of pharmaceutical compounds in the investigated secondary effluent were determined by LC-QTRAP-MS/MS, as well as their concentration in the permeate obtained in two selected experiments (UF4 and NF7, which were performed with the membranes PT and HL respectively). The

Table 6

Concentration of pharmaceutical compounds present in the secondary effluent and rejection coefficients obtained in experiments UF4 and NF7.

Pharmaceuticals	$[P]_0$ (ng L^{-1})	f_p (%) ^a	f_p (%) ^b
4-Amino-antipyrine (4-AA)	136	81	89
Antipyrine	140	54	82
Atenolol	1435	11	76
Benzafibrate	288	70	91
Carbamazepine	169	56	81
Ciprofloxacin	229	65	nd
Codeine	5794	79	94
Diclofenac	942	71	92
Fenofibric acid	180	86	88
Furosemide	451	70	78
Gemfibrozil	1280	59	85
Hydrochlorothiazide	2358	44	56
Ibuprofen	381	69	88
Iopamidol	2831	nd	64
Iopromide	2946	nd	86
Ketoprofen	607	58	87
Metronidazole	135	73	81
N-acetyl-4-amino-antipyrine (4-AAA)	5541	81	88
Naproxen	384	47	80
N-formyl-4-amino-antipyrine (4-FAA)	3432	51	87
Nicotine	122	60	81
Ofloxacin	285	nd	95
Pravastatin	136	73	95
Primidone	117	25	72
Ranitidine	225	28	75
Sulfamethoxazole	363	87	95
Trimethoprim	521	74	86
Velafaxime	267	45	87

nd: not determined.

^a Experiment UF4: membrane PT, TMP = 6 bar, $v = 2 \text{ m s}^{-1}$, $T = 20^\circ \text{C}$.

^b Experiment NF74: membrane HL, TMP = 30 bar, $v = 2 \text{ m s}^{-1}$, $T = 20^\circ \text{C}$.

results obtained for these concentrations of different families of pharmaceuticals in the secondary effluent and for the rejection coefficients of each compound determined in both experiments are summarized in Table 6. As can be observed, the retention of pharmaceuticals was higher for the NF HL membrane, as corresponds to its lower MWCO. The values of rejection coefficients covers a wide range (from 11 to 87% and from 56 to 95% for the PT and HL membranes respectively) because there are several solute properties that affect the retention (MW, molecular size, pK_a , $\log K_{ow}$, dipole moment, etc.) by different mechanisms (adsorption, steric hindrance, electrostatic repulsion, etc.) as has been discussed. Nevertheless, most of the pharmaceuticals presented retentions above 80% with the HL membrane.

In conclusion, a NF step with the HL membrane removes most of the organic compounds, including toxic pharmaceuticals, from the secondary effluent, being an excellent option for its purification before discharge. Further investigation is required to elucidate the retention mechanism for each specific compound and to establish a relation between the retention and the physical-chemical properties of the pharmaceuticals.

4. Conclusions

From the results obtained in the UF and NF experiments of secondary effluent from a WWTP in batch concentration mode, it was found that flux decline, and therefore membrane fouling, were higher for UF membranes. This permeate flux decline could be explained by the resistances in model series. In general, the contribution of the fouling resistance to the total resistance was lower than the inherent resistance of the membrane. Higher fouling resistances were found in membranes with high MWCO and in the case of the hydrophobic NF CK membrane. In addition, while the contribution of both internal (pore blocking and adsorption) and external (cake formation) fouling were similar in the selected UF

membranes, only external fouling was important in the filtration with NF membranes. With respect to the influence of the operating variables, although the permeate flux increased with the increase in the applied TMP, external fouling was also more pronounced, specially in membranes with higher MWCO. The tangential velocity or feed flow rate exerted a positive influence on the permeate flux, reducing external membrane fouling due to the increment of the turbulence at the membrane interface.

The evaluation of the rejection coefficients for the selected water quality parameters provided the following sequence: turbidity > absorbance at 254 nm > COD > TOC ≈ phosphorus > nitrogen for UF; and absorbance at 254 nm > phosphorus ≈ COD > TOC > turbidity > nitrogen for NF. These filtration processes led to moderate (UF) or high (NF) removal of organic compounds as well as of total phosphorus. On the contrary the elimination of total nitrogen was rather limited, specially in UF. At the same time, total removal of coliforms was achieved by both UF and NF. In addition, a high removal of pharmaceutical compounds present in the secondary effluent was obtained, specially with the NF HL membrane, which provided retention coefficients above 80% for most of the pharmaceuticals. Therefore, UF and NF are plausible options for the treatment of secondary effluents in order to obtain a permeate with good physico-chemical and microbiological quality, which can be reused in several applications. Specially interesting are the results obtained with the application of the NF HL membrane, which provided high permeate fluxes, a relatively low fouling, and high retention of contaminants.

Acknowledgements

This research was supported by the Ministerio de Ciencia e Innovación of Spain through the Projects CONSOLIDER-INGENIO CSD2006-00044 and CTQ 2007-60255. Authors wish to thank to M.J. Gomez from the University of Almeria for the analysis of pharmaceuticals.

References

- [1] M. Gomez, F. Plaza, G. Garralon, J. Perez, M.A. Gomez, A comparative study of tertiary wastewater treatment by physico-chemical-UV process and macrofiltration-ultrafiltration technologies, *Desalination* 202 (2007) 369–376.
- [2] U. Goren, A. Aharoni, M. Kummel, R. Messalen, I. Mukmenev, A. Brenner, V. Gitis, Role of membrane pore size in tertiary flocculation/adsorption/ultrafiltration treatment of municipal wastewater, *Sep. Purif. Technol.* 61 (2008) 193–203.
- [3] A. Lonigro, A. Pollice, R. Spinelli, F. Berrilli, D. Di Cave, C. D'Orazi, P. Cavallo, O. Brandonisio, *Giardia cyst* and *Cryptosporidium oocyst* in membrane-filtered municipal wastewater used for irrigation, *Appl. Environ. Microbiol.* 72 (2006) 7916–7918.
- [4] J. Gong, Y. Liu, X. Sun, O₃ and UV/O₃ oxidation of organic constituents of biotreated municipal wastewater, *Water Res.* 42 (2008) 1238–1244.
- [5] N.M. Al-Bastaki, Performance of advanced methods for treatment of wastewater: UV/TiO₂, RO and UF, *Chem. Eng. Process.* 43 (2004) 935–940.
- [6] J. Illueca-Muñoz, J.A. Mendoza-Roca, A. Iborra-Clar, A. Bes-Pia, V. Fajardo-Montañana, F.J. Martinez-Francisco, I. Bernacer-Bonora, Study of different alternatives of tertiary treatments for wastewater reclamation to optimize the water quality for irrigation reuse, *Desalination* 222 (2008) 222–229.
- [7] J.-J. Qin, M. Htun Oo, H. Lee, R. Kolkman, Dead-end ultrafiltration for pre-treatment of RO in reclamation of municipal wastewater effluent, *J. Membr. Sci.* 243 (2004) 107–113.
- [8] T. Wintgens, T. Melin, A. Schafer, S. Khan, S. Muston, D. Bixio, C. Thoeve, The role of membrane processes in municipal wastewater reclamation and reuse, *Desalination* 178 (2005) 1–11.
- [9] H.A. Mousa, S.A. Al-Hitmi, Treatability of wastewater and membrane fouling, *Desalination* 217 (2007) 65–73.
- [10] X. Wang, L. Wang, Y. Liu, W. Duan, Ozonation pre-treatment for ultrafiltration of the secondary effluent, *J. Membr. Sci.* 287 (2007) 187–191.
- [11] J. Haberkamp, M. Ernst, U. Bockelmann, U. Szewzyk, M. Jekel, Complexity of ultrafiltration membrane fouling caused by macromolecular dissolved organic compounds in secondary effluents, *Water Res.* 42 (2008) 3153–3161.
- [12] M.R. Wiesner, P. Aptel, Mass transport and permeate flux and fouling in pressure-driven processes, in: J.P. Mallevalle, E. Odendaal, M.R. Wiesner (Eds.), *Water Treatment Membrane Processes*, McGraw-Hill, New York, 1996.
- [13] S.F.E. Boerlage, M.D. Kennedy, M.R. Dickson, D.E.Y. El-Hodali, J.C. Schippers, The modified fouling index using ultrafiltration membranes (MFO-UF): characteristics, filtration mechanisms and proposed reference membrane, *J. Membr. Sci.* 197 (2002) 1–21.
- [14] F.J. Benitez, J.L. Acero, A.I. Leal, M. Gonzalez, The use of ultrafiltration and nanofiltration for the purification of cork processing wastewater, *J. Hazard. Mater.* 162 (2009) 1438–1445.
- [15] N. Park, Y. Lee, S. Lee, J. Cho, Removal of taste and odor model compound (2,4,6-trichloroanisole) by tight ultrafiltration membranes, *Desalination* 212 (2007) 28–36.
- [16] X. Jin, J. Hu, S.L. Ong, Influence of dissolved organic matter on estrone removal by NF membranes and the role of their structure, *Water Res.* 41 (2007) 3077–3088.
- [17] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G. Amy, B. Van der Bruggen, J.C. Van Dijk, Nanofiltration as a treatment method for the removal of pesticides from groundwater, *Water Res.* 41 (2007) 139–147.
- [18] Y. Zhang, B. Van der Bruggen, G.X. Chen, L. Braeken, C. Vandecasteele, Removal of pesticides by nanofiltration: effect of the water matrix, *Sep. Purif. Technol.* 38 (2004) 163–172.
- [19] A. Al-Amoudi, P. Williams, S. Mandele, R.W. Lovitt, Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability, *Sep. Purif. Technol.* 54 (2007) 234–240.
- [20] L.S. Clesceri, A.E. Greenberg, R.R. Trussell, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., APHA, AWWA, WPCF, Washington, DC, 1989.
- [21] M.J. Martinez-Bueno, A. Aguera, M.J. Gomez, M.D. Hernando, J.F. Garcia-Reyes, A. Fernandez-Alba, Application of liquid chromatography/quadrupole-linear ion trap mass spectrometry and time-of-flight mass spectrometry to the determination of pharmaceuticals and related contaminants in wastewater, *Anal. Chem.* 79 (2007) 9372–9384.
- [22] R. Fugere, N. Mameri, J.E. Gallot, Y. Comeau, Treatment of pig farm effluents by ultrafiltration, *J. Membr. Sci.* 255 (2005) 225–231.
- [23] S.-H. Kim, S.-Y. Moon, C.-H. Yoon, S.-K. Yim, J.-W. Cho, Role of coagulation in membrane filtration of wastewater for reuse, *Desalination* 173 (2005) 301–307.
- [24] A. Cassano, L. Donato, E. Drioli, Ultrafiltration of kiwifruit juice: operating parameters, juice quality and membrane fouling, *J. Food Eng.* 79 (2007) 613–621.
- [25] L. Fan, T. Nguyen, F.A. Roddick, J.L. Harris, Low-pressure membrane filtration of secondary effluent in water reuse: pre-treatment for fouling reduction, *J. Membr. Sci.* 320 (2008) 135–142.
- [26] I. Koyuncu, D. Topacik, Effect of organic ion on the separation of salts by nanofiltration membranes, *J. Membr. Sci.* 195 (2002) 247–263.
- [27] P. Banerjee, S. Das Gupta, S. De, Removal of dye from aqueous solution using a combination of advanced oxidation process and nanofiltration, *J. Hazard. Mater.* 140 (2007) 95–103.
- [28] M. Minhalma, M.N. De Pinho, Flocculation/flotation/ultrafiltration integrated process for the treatment of cork processing wastewaters, *Environ. Sci. Technol.* 35 (2001) 4916–4921.
- [29] D. Abdessemed, G.L. Nezzal, R. Ben Aim, Treatment of wastewater by ultrafiltration, *Desalination* 126 (1999) 1–5.
- [30] N. Mameri, F. Halet, M. Drouiche, H. Grib, H. Lounici, A. Paus, D. Piron, D. Belhocine, Treatment of olive mill washing water by ultrafiltration, *Can. J. Chem. Eng.* 78 (2000) 590–595.
- [31] M. Manttari, M. Kuosa, J. Kallas, M. Nystrom, Membrane filtration and ozone treatment of biologically treated effluents from the pulp and paper industry, *J. Membr. Sci.* 309 (2008) 112–119.
- [32] B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, *J. Membr. Sci.* 156 (1999) 29–41.
- [33] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review, *Water Res.* 38 (2004) 2795–2809.
- [34] K. Jarusutthirak, G. Amy, J.-P. Croue, Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes, *Desalination* 145 (2002) 247–255.