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USE OF ULTRAFILTRATION AND NANOFILTRATION PROCESSES FOR THE ELIMINATION OF THREE SELECTED EMERGING CONTAMINANTS: AMITRIPTYLINE HYDROCHLORIDE, METHYL SALICYLATE AND 2-PHENOXYETHANOL

Three emerging contaminants: amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE) were treated by means of filtration processes for their elimination from ultrapure (UP) water in a first stage, and from three water matrices (surface water from a reservoir, and two effluents from two municipal wastewater treatment plants) in a second stage. For this purpose, ultrafiltration and nanofiltration membranes were used in a cross-flow laboratory equipment. The permeate fluxes at the steady state were determined, and the resistances to the permeate flux were established. It was found that the inherent resistance of the clean membranes provided a much larger resistance than the fouling resistance. The retention coefficients for each individual contaminant were evaluated, as well as the retention coefficients referred to three water quality parameters: absorbance at 254 nm, COD and TOC. These parameters provide the effectiveness of the filtration processes for the elimination of the organic matter present in the selected water matrices.

1. INTRODUCTION

At recent times, an increasing public health concern has grown in relation to a new group of hazard pollutants that are frequently present in water systems, since little is known about their potential effects in humans and animals. The referred compounds are commonly known as emerging contaminants (ECs), because they are still unregulated or in the process of being regulated. This group is constituted by numerous chemical substances including nanomaterials, pesticides, pharmaceuticals and personal care products, industrial compounds, fragrances water treatment by-products, flame retardants

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surfactants, etc. [1]. They can be found in surface and ground waters, and even in drinking water [2–5], being their main source municipal treated wastewater, due to the fact that wastewater treatment plant (WWTP) technologies are very often unable to entirely degrade such persistent pollutants. As these ECs constitute a potential risk for human health, since they can cause unexpected physiological consequences, their elimination from waters together with other priority pollutants is an important goal in environmental issues.

Due to this concern, and among other technologies, membrane processes employing ultrafiltration (UF) and nanofiltration (NF) membranes are increasingly used in wastewater reclamation to remove micropollutants in general, and ECs in particular, as well as natural organic matter (NOM) [6–8]. In effect, retention of organic micropollutants by UF membranes is attributed to several causes: adsorption on the membrane during the early stages of filtration, or to interactions with the membrane fouling layer, and/or interactions with dissolved NOM in solution [9]. On the other hand, NF membranes remove organic solutes by three main mechanisms, i.e., size exclusion, electrostatic repulsion and adsorption [10, 11].

According to these considerations, the present research was designed for the specific elimination of three frequently found emerging contaminants in water systems by means of UF and NF membranes. These ECs selected were: amitriptyline hydrochloride (AH), methyl salicylate (MS) and 2-phenoxyethanol (PE). Specifically, amitriptyline hydrochloride is the most widely used tricyclic antidepressant. Its mechanism of action involves the inhibition of reuptake of norepinephrine and serotonin. Methyl salicylate is a salicylic acid derivative, naturally produced by many species of plants, although nowadays it is industrially produced by esterification of the acid with methanol. At high concentrations, this drug acts as a rubefacient, analgesic, and anti-inflammatory. Finally, 2-phenoxyethanol is a bactericide generally combined with quaternary ammonium compounds. It is often used in dermatological products such as skin creams and sunscreens; and also, as a fixative for perfumes, insecticides, and topical antiseptics.

Although some information on the elimination of ECs by filtration processes can be found in the literature, no studies on the elimination of these specific emerging contaminants, which are selected in this research, have been provided. Then, in the first stage of this work, the selected ECs were dissolved in ultrapure (UP) water and subjected to UF and NF experiments. Similarly, in the second stage, they were dissolved in various real water matrices in order to reproduce more realistic conditions as those carried in treatments plant. With the results obtained, several objectives are pursued: the study of the evolution of the permeate flux with filtration time and volume retention factors; the establishment of the effect of several operating parameters (pH and nature and molecular weight cut-off (MWCO) of the membranes) on the steady-state permeate flux; the evaluation of the partial contribution of different membrane resistances to the total resistance; and the determination of retention coefficients for each EC. Finally, the influence of the presence of natural organic matter in the water matrices on the filtration process has also been established.

2. MATERIALS AND METHODS

Model compounds, membranes and water systems. Selected ECs (PE, MS and AH) were purchased from Sigma-Aldrich (Germany) with the highest purity available. Table 1 summarizes the molecular structures and molecular weights (*MW*) of these model compounds, as well as their pK_a values and the $\log K_{ow}$ values, which constitute a measure of their hydrophobic/hydrophilic character.

Table 1

Physicochemical properties of model compounds

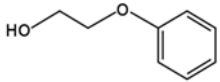
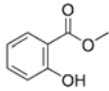
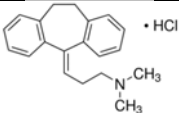
Emerging contaminant	Chemical structure	<i>MW</i> , g·mol ⁻¹	pK_a	$\log K_{ow}$
2-phenoxyethanol (PE)		138.17	–	1.16
Methyl salicylate (MS)		152.15	9.87	2.55
Amitriptyline hydrochloride (AH)		313.87	9.4	5

Table 2

Properties of target membranes

Membrane	Material	MWCO [Da]	pH range	<i>PWP</i> [dm ³ ·h ⁻¹ ·m ⁻² ·MPa ⁻¹]
PW (UF)	PES	20 000	2–11	776
PT (UF)		5000	2–11	213
GK (UF)	TF	2000	2–11	68
HL (NF)	PTFE	150–300	3–9	125
DL (NF)		340	2–11	26
CK (NF)	CA	150–300	2–8	24

Table 2 summarizes commercial selected membranes used. They were flat-sheet membranes provided by the GE Osmonics Inc. (Florida, USA), with the same effective surface area of 28 cm² in all membranes. In the UF process, the three membranes are commercially called PW, PT, and GK, with molecular weight cut-off (MWCO) of 20 000, 5000 and 2000 Da, respectively. The NF membranes are commercially called HL, DL, and CK, all of them with similar MWCO in the range 150–340 Da, according to the data provided by the manufacturer. The nature of these membranes was as follows: the GK membrane was a thin film composite membrane, with a cross-linked aromatic polyamide top layer,

while the PT and PW membranes were made of polyethersulfone. All of them presented a hydrophilic character. Regarding to the NF membranes, the DL and HL were made of thin film composite (polypyperazinamide skin layer on a polyester support), and the CK was of cellulose acetate. According to previous studies [12, 13] which measured their contact angles, polyamide membranes were less hydrophobic than polyethersulfone membranes.

Table 3

Quality parameters of selected real water matrices

Parameter	PA	LA	BA
pH	7.4	7.9	8.3
Conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$	80	570	550
A254 nm, cm^{-1}	0.187	0.041	0.245
COD, $\text{mg O}_2\cdot\text{dm}^{-3}$	18	7	56
Alkalinity, $\text{mg CaCO}_3\cdot\text{dm}^{-3}$	30	335	325
TOC, $\text{mg C}\cdot\text{dm}^{-3}$	5.2	2.9	11.1
Total nitrogen, $\text{mg N}\cdot\text{dm}^{-3}$	1.51	21.3	35.5
Total phosphorus, $\text{mg P}\cdot\text{dm}^{-3}$	0.041	0.156	1.76

As mentioned previously, the filtration experiments were carried out with the ECs dissolved in UP water, and also, by using several water matrices, in order to reproduce more realistic water treatment conditions. These aquatic systems whose main quality parameters are compiled in Table 3, were the following: a surface water collected from the public reservoir Peña del Aguila (PA), located in the Extremadura Community, south-west of Spain, and two secondary effluents from WWTPs corresponding to the cities of Badajoz (BA) and La Albuera (LA), also in the Extremadura Community. These water systems were filtered through a $0.45\ \mu\text{m}$ cellulose nitrate filter within the first 24 h after collection and stored at $4\ ^\circ\text{C}$ until use. Specifically, UV absorbance and TOC content constitute a significant index of the total dissolved organic matter (DOM) present in these effluents, which has a great influence on the performance of various filtration processes. In all cases, the solutions were prepared by dissolving the ECs ($1\ \mu\text{mol}\cdot\text{dm}^{-3}$ of each) in UP water (from a Milli-Q system, Millipore Ibérica, Spain) or in the three real water matrices selected.

Experimental equipment and procedures. In the experiments, a laboratory membrane filtration unit model P-28TM was used supplied by the CM-CELFA Membrantech-nik AG (Seewen, Switzerland), operating in cross-flow mode (feed stream flowing tangentially to the membrane surface). It was constituted by a $500\ \text{cm}^3$ pressurized storage vessel and a gear pump which fed the solution to the flat-sheet membrane module at the desired flow rates. Additional details of this equipment were provided elsewhere [14].

During each experiment, the permeate stream was collected separately and its cumulative volume was measured with a Mettler balance. At the same time, the retentate stream was recycled to the feed tank, and therefore, a batch concentration mode was followed. The tangential velocity ($1 \text{ m} \cdot \text{s}^{-1}$) and transmembrane pressure (TMP, 0.3 MPa in the UF experiments and 2 MPa in the NF experiments) were remained constant. This TMP was controlled by feeding nitrogen gas to the head of the storage vessel.

A new membrane was used for every experiment conducted, and the operating protocol consisted in the following stages: firstly, ultrapure water was filtered for 3 h, and the water permeate flux (J_w) was measured in order to determine the membrane hydraulic permeability (PWP) as will be discussed later. The second stage consisted in the filtration experiments of the ECs solutions (300 cm^3), where the model compounds were dissolved in UP or in the water matrices ($1 \text{ } \mu\text{mol} \cdot \text{dm}^{-3}$ for each compound). During these experiments, the permeate was regularly collected for the determination of the pollutants permeate flux (J_v). At the same time, samples of the feed, retentate and permeate streams were collected for the analysis and measurement of the ECs concentrations. Additionally, in the case of the real water matrices, the following global quality parameters were also evaluated: absorbance at 254 nm, COD and TOC. The experiments ended when a volume reduction factor (VRF) around 3 was reached. Once the filtration of ECs was ended, the feed tank was emptied and filled with UP water in a third stage, and then the membrane was rinsed by filtrating UP water again. In this way, the cake layer formed on the membrane surface was removed, and the final pure water flux was again measured, as will be explained in the Discussion Section.

Analytical methods. The three selected ECs were analysed by HPLC using a Waters chromatograph (Alliance 2695) equipped with a 996 photodiode array detector and a Waters Nova-Pak C18 column ($5 \text{ } \mu\text{m}$, $150 \times 3.9 \text{ mm}$). The detection was performed at 238 nm for AH and MS, and 220 nm for PE. The mobile phase was a mixture of methanol and $0.01 \text{ mol} \cdot \text{dm}^{-3}$ aqueous phosphoric acid solution, operating in a gradient mode. The elution flow rate was $1 \text{ cm}^3 \cdot \text{min}^{-1}$ and the injection volume was $100 \text{ } \mu\text{l}$ in all samples.

The analytical methods for the characterization of the selected water matrices were followed according to the Standard Methods [15]. TOC was determined by using a total organic carbon analyzer TOC-multi N/C 3100 (Analytik Jena). Absorbance at 254 nm was measured by means of a spectrophotometer Unicam Helios Beta, and COD was determined by using Dr. Lange kits.

Theoretical calculations. In a filtration process, the permeate flux (J_w in the case of UP water, or J_v in the aqueous solutions of ECs dissolved in UP water, synthetic water or real water matrices) ($\text{dm}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$) was determined by using the expression:

$$J_i = \frac{\Delta V_p}{\Delta t A}, \quad i = w, v \quad (1)$$

where ΔV_p represents the cumulative permeate volume difference (dm^3), Δt is the time difference (h) and A is the membrane surface area (m^2). The water permeate fluxes J_w are used for the later determination of hydraulic permeability PWP ($\text{dm}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2} \cdot \text{MPa}^{-1}$) of the membranes by means of the following equation:

$$PWP = \frac{J_w}{TMP} \quad (2)$$

The volume reduction factor (VRF) is defined as the ratio between the feed volume V_f (dm^3) and the retentate volume $V_r = V_f - V_p$ (dm^3), and can be calculated by using the equation:

$$VRF = \frac{V_f}{V_r} \quad (3)$$

Regarding to the resistances to the permeate flux, the total hydraulic resistance R_t (m^{-1}) was evaluated from the permeate flux J_v , according to the general Darcy's law [6]:

$$R_t = \frac{TMP}{\mu J_v} \quad (4)$$

where TMP is the transmembrane pressure (MPa), and μ is the solution viscosity (μ_w in the case of UP water, or μ in the aqueous solutions of ECs dissolved in UP water, synthetic water or real water matrices, which were experimentally measured) ($\text{m}^2 \cdot \text{h}^{-1}$). This R_t is the result of several resistances in a series:

$$R_t = R_m + R_f = R_m + R_{if} + R_{ef} \quad (5)$$

where R_m is the intrinsic resistance of clean membrane, and R_f is the fouling resistance with two components, the internal (R_{if}) and external (R_{ef}) fouling (all resistances in m^{-1}).

One of the parameters which best provide the efficiency of a membrane in a filtration process is the retention coefficient, which was determined for the selected ECs by the equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (6)$$

where C_f and C_p are the concentrations of each EC ($\text{mol}\cdot\text{dm}^{-3}$) in the feed and permeate streams, respectively. Similarly, the retention coefficients were evaluated for the water quality parameters selected in the present work. For the specific case of COD ($\text{mg O}_2\cdot\text{dm}^{-3}$), this coefficient was defined by the expression:

$$R_{\text{COD}} = \frac{\text{COD}_f - \text{COD}_p}{\text{COD}_p} \times 100\% \quad (7)$$

where COD_f and COD_p represent the COD ($\text{mg O}_2\cdot\text{dm}^{-3}$) in the feed and permeate streams, respectively. Similar equations were used for TOC (R_{TOC}), and UV absorbance at 254 nm (R_{254}).

3. RESULTS AND DISCUSSION

3.1. WATER PERMEABILITY OF THE MEMBRANES

Firstly, the filtration of pure water through the selected membranes was conducted, in order to evaluate the hydraulic permeability (PWP) of the membranes. For this purpose, the water permeate volume (V_p) was continuously measured through each experiment, and the water permeate flux (J_w) was determined by means of Eq. (1). Once the water permeate fluxes J_w were determined for each membrane, the values for PWP were deduced by using Eq. (2). These PWP values obtained for the selected membranes are also summarized in Table 2. As is observed, an increase in the hydraulic permeability is clearly obtained with the increase in the MWCO in the UF membranes, as could be expected, because larger pore sizes lead to higher pure water fluxes. However, in the NF membranes, as the membranes have similar MWCO, different properties are responsible for the PWP values: in addition to MWCO, the internal structure and composition of the membrane, and their morphology and hydrophobicity/hydrophilicity also contribute to PWP . They can explain the lower PWP values obtained for the CK and DL membrane in comparison to the HL membrane, whose higher PWP value has also been reported in previous works [16, 17].

3.2. FILTRATION OF ECs IN UP WATER

The selected ECs dissolved together in UP water were subjected to filtration experiments by using the UF and NF membranes already described. The operating conditions (TMP and pH) applied to specific experiments were varied according to the values summarized in Table 4. These pH values were adjusted by means of phosphoric acid/phosphate buffer ($0.01 \text{ mol}\cdot\text{dm}^{-3}$) and also remained constant during the whole experiment.

Table 4

Filtration experiments performed with ECs dissolved in UP water and real water matrices

Experiment	Membrane	TPM [MPa]	pH	J_{vss} [$\text{dm}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$]
UPUF-1	GK	0.3	7	16.5
UPUF-2	PT		3	57.8
UPUF-3			5	57.2
UPUF-4			7	56.7
UPUF-5			9	54.5
UPUF-6	PW		7	185.8
UPNF-1	HL	2	3	138.4
UPNF-2			5	137.1
UPNF-3			7	138.1
UPNF-4			9	138.4
UPNF-5			7	41.6
UPNF-6			7	54.9
PAUF	PT	0.3	7.2	54.9
LAUF			8.1	61.3
BAUF			8.5	49.8
PANF	HL	2	7.2	119.1
LANF			8.1	123.2
BANF			8.5	117.6

It must be taken into account the VRF factor, already defined by Eq. (3). As was previously noted, the experiments ended when VRF was around 3, that is, when volumes around 200 and 100 cm^3 were collected for permeate and retentate streams, respectively.

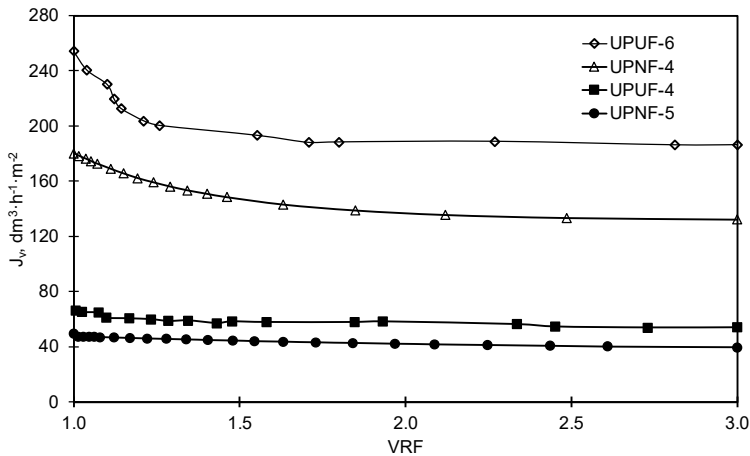


Fig. 1. Evolution of the permeate flux with VRF during the filtration of emerging contaminants dissolved in UP water (UPUF-4, UPUF-6, UPNF-4 and UPNF-5)

In the filtration experiments of ECs, the permeate flux of the solutions (now represented by J_v) was measured at time intervals by means of Eq. (1), where J_w is substituted by J_v . The J_v evolution with VRF is represented in Fig. 1 for several experiments taken as examples, being the same performance in the remaining experiments. It revealed that there was an initial decrease in J_v with the increase of VRF ; and later, this permeate flux remained almost constant. This permeate flux decay is a consequence of the increasing membrane fouling, which can be due to different causes, such as pore blocking or adsorption of solutes onto the membranes [18–20]. In this case, where model compounds dissolved in UP water with low concentrations are processed, the fouling effect is generally low, and therefore, the decay is probably due to adsorption of the ECs on the membrane. The mentioned constant permeate flux is obtained around $VRF = 3$ in most of the experiments carried out, and consequently, it is considered as the steady-state permeate flux (J_{vss}), whose values for all the experiments conducted, are also compiled in Table 4.

Focusing in these values of J_{vss} , it can be observed that they are affected by the operating parameters. Thus, a direct influence of the MWCO on J_{vss} is clearly deduced in the UF process: in effect, at pH = 7 and TMP = 0.3 MPa, there was an increase of the permeate flux when increasing the MWCO of the selected membranes (Expts. UPUF-1, UPUF-4 and UPUF-6), with values of 16.5, 56.7 and 185.8 dm³ h⁻¹ m⁻² for GK, PT and PW membranes, respectively. These results are due to the fact that a membrane with lower MWCO presents a greater resistance for the solution to cross the membrane; and consequently, lower permeate fluxes are obtained. In the NF process no conclusion could be drawn based on the MWCO, because these membranes had the same nominal pore size (in the range 150–340 Da). However, the results indicate that at similar operating conditions, the HL membrane presented a higher permeate flux than the CK or DL membranes: 138.1 vs. 41.6 and 54.9 dm³ h⁻¹ m⁻² (expts. UPNF-3, UPNF-5 and UPNF-6). These differences are a consequence of the different nature of the membranes, and agree with the results previously reported and discussed for *PWP*, where the hydraulic permeability was much higher for the HL membrane than for the CK and DL membranes. On the other hand, and regarding to the pH influence, the UF PT membrane presents a very slight decrease in J_{vss} with the increase in the pH (Expts. UPUF-2, UPUF-3, UPUF-4, and UPUF-5); however, this effect is almost negligible in the NF HL membrane (Expts. UPNF-1, UPNF-2, UPNF-4, and UPNF-4).

The permeate flux decline already commented is a consequence of the resistances found by the solutions to pass through the membranes. This decline can be analysed by means of the resistances in series model. This model and their different resistances being described in a preceding section (Eqs. (4) and (5)).

The values of the mentioned resistances were determined according to the experimental protocol described in the experimental section: thus, R_m was evaluated by using Eq. (4) when applied to the filtration experiments of UP water with each new membrane. Obviously, the viscosity and permeate flux in that Eq. (4) corresponded to those of the

UP water (μ_w and J_w). Similarly, R_t was also determined by means of Eq. (4) applied to the filtration experiments of the ECs aqueous solutions. In that case, the viscosity and the permeate flux of the solutions (μ and J_v) were used and R_f was calculated from Eq. (5), as the difference between R_t and R_m . Finally, the internal fouling resistance R_{if} was evaluated from the final filtration stage of UP water that removed the cake layer formed, but not the pore blocking. For this purpose, Eq. (4) was again applied to the water permeate flux J_w obtained in this last stage. The difference between R_f and R_{if} provided the values of the external fouling resistance R_{ef} . Following this procedure, the values obtained for these resistances in all the experiments conducted are summarized in Table 5, which also shows the ratio R_f/R_t , which indicates the partial contribution of the fouling resistance to the total resistance.

Table 5

Resistances in the filtration of Ecs dissolved in different matrices at $VRf = 3$

Experiment	Membrane	$R_t \times 10^{-13}$ [m ⁻¹]	$R_m \times 10^{-13}$ [m ⁻¹]	$R_f \times 10^{-13}$ [m ⁻¹]	$R_{ef} \times 10^{-13}$ [m ⁻¹]	$R_{if} \times 10^{-13}$ [m ⁻¹]	R_f/R_t [%]
UPUF-1	GK	6.56	5.31	1.25	0.96	0.29	19.1
UPUF-2	PT	1.87	1.62	0.25	0.22	0.04	13.5
UPUF-3	PT	1.93	1.68	0.25	0.19	0.06	12.9
UPUF-4	PT	1.91	1.70	0.21	0.12	0.09	11.0
UPUF-5	PT	1.98	1.79	0.19	0.17	0.02	9.6
UPUF-6	PW	0.58	0.46	0.12	0.11	0.01	20.2
UPNF-1	HL	6.60	3.41	3.20	2.89	0.31	48.4
UPNF-2	HL	5.31	3.64	1.67	1.54	0.13	31.5
UPNF-3	HL	4.24	2.96	1.28	1.09	0.19	30.2
UPNF-4	HL	3.85	2.20	1.65	1.44	0.21	42.9
UPNF-5	CK	18.2	14.6	3.59	3.22	0.37	19.7
UPNF-6	DL	13.41	11.1	2.34	1.83	0.51	17.4
PAUF	PT	1.97	1.68	0.29	0.10	0.19	14.8
LAUF	PT	1.94	1.78	0.16	0.10	0.06	8.2
BAUF	PT	2.71	2.02	0.70	0.31	0.38	25.7
PANF	HL	3.89	3.66	0.23	0.20	0.03	5.9
LANF	HL	4.26	3.66	0.60	0.33	0.27	14.0
BANF	HL	5.31	4.06	1.25	0.93	0.33	23.6

The analysis of the total resistance R_t (Table 5) shows that the higher values in the UF process corresponded to the GK membrane ($R_t = 6.56 \times 10^{13} \text{ m}^{-1}$ in expt. UPUF-1); and the lower value corresponded to the PW membrane ($R_t = 0.58 \times 10^{13} \text{ m}^{-1}$ in expt. UPUF-6), as a direct consequence of the increasing MWCO (2000 and 20 000 Da for GK and PW membranes, respectively). Similarly, this effect was also observed for the fouling resistance R_f in these UF membranes with greater values with lower MWCO. Thus, the GK membrane presented the highest value of R_f (expt. UPUF-1), while the

PW membrane presented the lowest one (expt. UPUF-6). In the case of the NF membranes, it is easily observed that the values of the total resistance R_t , membrane resistance R_m , and fouling resistance R_f were globally much higher than in the UF process as could be expected. As the MWCO is almost the same in these three membranes, the differences in the values can be again attributed to their different natures. Once again, the R_t , R_m and R_f resistances are in the same range for CK and DL membranes (expts. UPNF-5 and UPNF-6), while the HL membrane provided lower values (expt. UPNF-3): as discussed previously, higher permeate fluxes were generated in this membrane as a consequence of its lower resistances. On the contrary, CK and DL presented lower permeate fluxes due to their higher resistances.

The comparison between R_f and R_m showed in all cases that R_f is smaller than R_m ; that is, the partial contribution of the fouling resistance to the total resistance given by the ratio R_f/R_t in Table 5, is lower than 20% in the UF experiments; and in the range 20–50% in the NF experiments. Consequently, the contribution of the inherent membrane resistance R_m is higher in comparison to the fouling resistance R_f , which confirms that the membrane fouling is generally low in such as kind of experiments where model ECs are dissolved in UP water. A contrary effect was observed in filtration experiments of industrial wastewaters [21], where the partial contribution of R_f to the total resistance R_t was much higher than the contribution of R_m , due to greater pollutant load in these waters, which fouled the membranes in a higher extent. Finally, with respect to the contribution of internal and external fouling to the total fouling, R_{ef} was higher than R_{if} for all the selected membranes, which indicates that polarization concentration and cake layer formation contribute to a higher extent to fouling than pore blocking and contaminants adsorption onto the membrane.

The retention coefficient constitutes an interesting parameter that provides information about the efficiency of a membrane in the filtration process of a specific solute. It relates the concentration of a substance in the permeate stream with its concentration in the feed stream, and can be determined for the selected ECs of the present work by Eq. (6). The R coefficients obtained decreased slightly with the increase in the VRF parameter during the experiment, and consequently, with processing time. This decay ended at VRF values around 3, and then, they are considered the R coefficients at steady-state conditions.

A wide range of results for these R coefficients was obtained in the experiments of the present study, results that are summarized in Fig. 2 for the membranes tested and selected ECs. By considering each specific compound, the NF process of AH provided the R coefficients with values around 100%; that is, this contaminant was almost totally retained with these membranes. In its UF process, AH also presented elevated R coefficients, although decreasing values with the increase in the MWCO. Intermediate values were deduced for MS (in the range 80–100% for NF membranes, and 65–78% for the UF membranes); and low R coefficients were obtained for PE, (30–60% for the NF membranes, and 25–38% for the UF membranes).

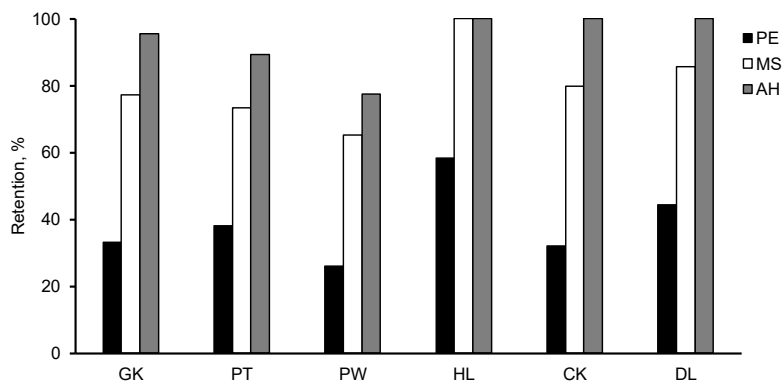


Fig. 2. Retention coefficients of emerging contaminants obtained with the different UF (PW, GK and PT) and NF (DL, CK and HL) membranes tested in UP water at $V/Rf = 3$ and $pH = 7$ (UPUF-1, UPUF-4, UPUF-6, UPNF-3, UPNF-5, and UPNF-6)

The high retention coefficients for the NF membranes could be expected as a consequence of their low MWCO [22]. In addition, among the UF experiments, the effect of the membrane MWCO can be also observed: thus, the GK membrane provided higher retentions than the PT membrane in the UF process (excepting for PE), while the PW membrane presented the lower R coefficients. However, since the MWCO of these UF membranes is much higher than the molecular weight of the selected pollutants, other mechanisms than size exclusion must also contribute efficiently to the retention of ECs. Specially, adsorption mechanism should be also responsible for this retention in addition to size exclusion: in effect, the highest values of the retention coefficients obtained for AH with the use of UF membranes is also a consequence of its hydrophobic nature, according to its high value of $\log K_{ow}$ summarized in Table 1 ($\log K_{ow} = 5.0$). Intermediate retentions were obtained for MS which also presents hydrophobic nature, although at a moderate level ($\log K_{ow} = 2.55$). On the contrary, PE is the most hydrophilic compound ($\log K_{ow} = 1.16$), and therefore it is only partially adsorbed onto the membranes, so that its retention is rather low.

In the case of the NF membranes, the differences between the R coefficients obtained for a specific compound are not attributed to the different values of membranes MWCO, since they are very similar. Then, additional considerations must be taken into account in order to explain the different retentions. Thus, on one hand, AH has a MW in the same range as the MWCO of the DL membrane, and slightly higher than those of the HL and CK membranes. Consequently, the size exclusion is the main mechanism responsible of the AH rejection, and the R values obtained are the highest (almost totally rejected). On the contrary, the MWCO of MS and PE are in the same range than the MWCO of these NF membranes, or even lower; and therefore, size exclusion mechanism contributes in a less extent, providing for both contaminants lower R values than for AH. In those cases, adsorption mechanism must be also responsible of retention for

MS and PE, as it occurred in UF process, with lower R values for PE due to its hydrophilic nature ($\log K_{ow} = 1.16$), and higher R values for MS due to its moderate hydrophobic character ($\log K_{ow} = 2.55$).

3.3. FILTRATION OF ECs IN REAL WATER MATRICES

The ECs were dissolved in the three selected water matrices (Table 3). UF experiments with the PT membrane and NF experiments with the HL membrane were performed at TMP and pH values (those of the natural water matrices) also summarized in Table 4. The results obtained for the steady-state permeate fluxes J_{vss} , measured at $VRF = 3$, are also shown in Table 4.

Firstly, it is again observed for these real waters that the NF process yielded higher J_{vss} values than the UF process. In addition, while values of J_{vss} in the same range are obtained in the UF process with the PT membrane for both, the UP water and the natural waters (see expts. UPUF-3, PAUF, LAUF and BAUF), the NF process with the HL membrane yielded lower J_{vss} values in the real waters (see expts. UPNF-3, PANF, LANF and BANF) with a flux decrease that was more pronounced in the real waters filtration process.

The influence of the water matrix on these J_{vss} can also be pointed out from the results shown in Table 4: thus, the trend obtained for the permeate J_{vss} is: LA > PA > BA. The decrease in the permeate flux trend agrees with the increase in the NOM present in the selected waters, which is measured by the values compiled in Table 3 for absorbance, and TOC and DOC contents. In effect, this increase in NOM induces several effects such as larger adsorption of species onto the membrane, pore blocking and formation of a cake layer on the membrane surface, all these effects leading to lower J_{vss} values. Consequently, LA water with lower NOM contents provided higher J_{vss} values; on the contrary, the higher values of absorbance, TOC and DOC contents in BA wastewater provided the lowest J_{vss} values. Obviously, the intermediate NOM content in the PA water led to intermediate J_{vss} values.

Similarly to the UF and NF experiments of ECs dissolved in UP water, the values of the resistances R_t , R_m and R_f were evaluated for both UF and NF filtration processes of the ECs dissolved in real water matrices. The values obtained are also shown in Table 5, which also compiles the partial contribution of the fouling resistance to the total resistance, represented by the term R_f/R_t . Once again, much lower contributions of R_f resistance to the total resistance R_t were observed (below 25% in all cases), as a consequence of the low fouling effect that occur in these systems, while the contribution of the membrane resistance R_m is higher (above 75% in all cases).

Similarly, the efficiency of the membranes for the retention of the selected pharmaceuticals when they are present in the waters tested was also determined by the evaluation of the retention coefficients. Figures 3a and 3b show the R values at $VRF = 3$, by repre-

senting the retention coefficients for the three compounds in both, the UF and NF processes with the PT and HL membranes, respectively. On one hand, the retentions were considerably higher in the NF process than in the UF process as a consequence of the lower MWCO of the CK membrane, as was already discussed for UP water. Additionally, the sequence of retentions already obtained for UP water was again confirmed: $AH > MS > PE$. On the other hand, by considering the nature of the water matrices, the retention coefficients for a specific compound reveal that slightly higher retentions were obtained in the municipal wastewater treatment plant BA, that was followed by the reservoir PA water, while lower values were obtained in the LA water. This effect could be expected according to the NOM contents shown in Table 3: the BA water, with higher NOM contents, induces higher fouling on the membranes due to adsorption and pore blocking; and this membrane fouling decreases the pore size and increases the ECs retention. Additionally, the formation of an organic layer (cake) on the membrane leads to the possibility that the adsorption of the pollutants on this layer increases their retention.

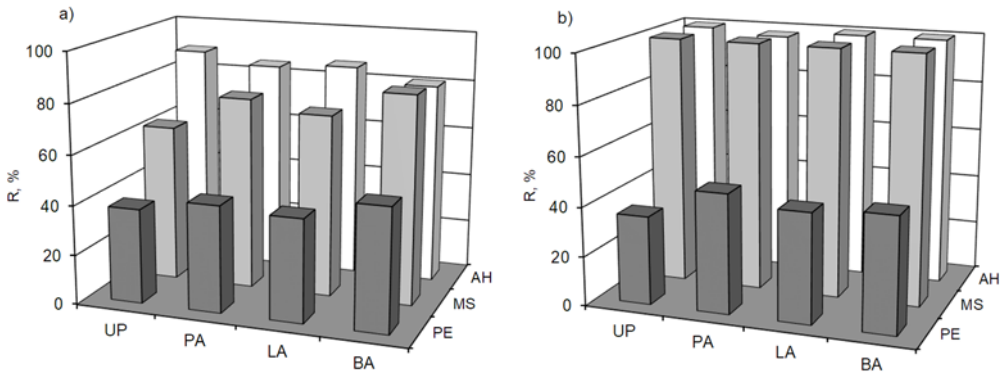


Fig. 3. Retention coefficients at $VRF = 3$ for three ECs in various water systems: a) UF experiments using the PT membrane, b) NF experiments using the HL membrane

Finally, the effectiveness of the filtration processes for the elimination of the organic matter present in these water matrices can be also evaluated by the retention coefficients referred to the selected water quality parameters: COD, and TOC, and absorbance at 254 nm (R_{COD} , R_{TOC} and R_{254} , respectively). These coefficients were evaluated for various filtration times by means of Eq. (7), and a slight decrease with filtration time was observed due to the increase of the concentration gradient, and consequently, to the decrease in the retention rate during the experiments because of the saturation of the membrane. At advanced processing times, around $VRF = 3$, the steady-state conditions were reached, and the values for the retention coefficients of these quality parameters are summarized in Table 6.

Table 6

Retention coefficients [%] for several quality parameters in filtration experiments with real waters at $VRF = 3$

Experiment	Membrane	R_{254}	R_{COD}	R_{TOC}
PAUF	PT	52.4	28.2	40.9
LAUF	PT	67.7	53.6	71.4
BAUF	PT	52.4	28.2	40.9
PANF	HL	87.8	53.8	76.8
LANF	HL	74.3	59.3	74.5
BANF	HL	100	51.2	92.3

Several facts can be deduced from these values in Table 6. On one hand, the retentions were higher in the NF process than in the UF process as a consequence of the lower MWCO of the HL membrane, as previously discussed for UP water. Thus, values in the ranges 40–71% for TOC, 28–53% for COD and 52–67% for absorbance, were obtained in the UF process. At the same time, values in the range 74–92% for TOC, 52–59% for COD and 74–100% for absorbance were obtained in the NF process. In conclusion, these filtration processes led to moderate (UF) and high (NF) elimination of the organic matter content present in the water matrices tested. Finally, the UF PT membrane provided lower retentions of the ECs in natural waters than in the filtration in UP water, because the NOM present in these waters competes with the ECs for the retention into the pores.

From these results, it can be qualitatively deduced that the HL membrane is adequate for the elimination of ECs from natural waters to produce drinking water, and for the purification of not very contaminated secondary effluents for reuse. However, the retentate stream that is generated constitutes a concentrated fraction with high content in hazardous materials, and needs additional treatments for its purification before its disposal, such as some chemical oxidation or physical treatments.

4. CONCLUSIONS

- A continuous decrease of the flux decline with processing time is observed, until an almost constant value was reached at volume reduction factor around 3.
- A direct influence of the MWCO on the values of the permeate flux at the steady state is deduced in the UF process, while these permeate fluxes are mainly affected by the nature of the membranes in the NF process.
- The calculated different types of resistances to the permeate flux reveal that the inherent resistance of the clean membranes is much larger than the fouling resistance.

• According to the values of the retention coefficients, the nanofiltration thin film composite membrane with MWCO ranging from 150 to 300 Da was the most appropriate for the removal of the selected emerging contaminants from the waters tested.

The above referred membrane also provided the high retention for absorbance at 254 (in the range 75–100%), and TOC (in the range 76–92%), and moderate for COD in the range (51–59%).

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