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# Retention of emerging micropollutants from UP water and a municipal secondary effluent by ultrafiltration and nanofiltration

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ABSTRACT

This study investigates the removal of 11 emerging contaminants dissolved in ultrapure water or in municipal secondary effluent by ultrafiltration and nanofiltration membranes. The influence of the most important operating variables (nature and MWCO of the membranes, transmembrane pressure, tangential velocity, pH and temperature) on the permeate flux and on the retention of the selected compounds was discussed. Most of the emerging compounds presented retentions above 70% with the selected NF membranes. However, lower retention coefficients were obtained with the UF membranes tested (<50%, except for hydroxybiphenyl). According to the results obtained for membrane fouling, retention coefficients and adsorption of contaminants on the membranes, while adsorption is the main mechanism for micropollutants retention by UF filtration membranes, size exclusion and electrostatic repulsion at high pH are dominant in the case of NF membranes. In addition, retention coefficients for parameters that measure the quality of the effluent (chemical oxygen demand, 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 municipal secondary effluent, leading to a permeate stream that can be reused in several applications.

## 1. Introduction

The increasing demand of water nowadays and the shortage in natural freshwater sources have forced to consider the great amounts of wastewaters generated worldwide as alternative water resources, by reusing them after the proper treatments. However, conventional water technologies have demonstrated in some cases their inability to remove all organic pollutants to levels less than the concentrations permitted by law regulations, as those required to prevent environmental damages. In this way, municipal wastewater constitutes an important source of possible water supply after purification in wastewater treatment plants (WWTP). However, they often contain more than 200 different chemical compounds, many of which are toxic to aquatic organisms and present risks to the health of men and animals. Although frequently at very low concentrations, among the organic compounds involved in this pollution, a wide group of emerging micropollutants has been detected in wastewater effluents, receiving waters, drinking water sources and some treated waters [1–4]. In that group, pesticides, pharmaceuticals, personal care products, fuel additives, flame-retardants, plasticizers and numerous other industrial pollutants are included. Frequently, their removal by conventional wastewater and drinking water processes has not been shown to be effective [5,6], and consequently, there is a need to investigate new technologies for their elimination.

Due to this concern, different physical–chemical processes have been proposed as tertiary treatment of secondary effluents from municipal treatment plants, such as activated carbon adsorption [7,8], advanced oxidation by ozone and hydroxyl radicals [9,10], photo-catalysis UV/$TiO_2$ [11], etc. More recently, membrane processes employing nanofiltration (NF) and ultrafiltration (UF) are increasingly used in wastewater reclamation and drinking water to remove micropollutants as well as natural organic matter [12–14]. On the contrary, the main disadvantage of these processes is membrane fouling, represented by the drop in the membrane flux with time [15], which is due to different mechanisms: adsorption of solutes onto the membrane, deposition of small colloidal particles on the membrane pores (pore blocking) and build up of particles in form of a cake layer. In spite of this disadvantages, the application of filtration techniques to WWTP effluents provides an important improvement in the quality of the permeate formed, making it suitable for latter uses [16].

The present research is focused in the assessment of the specific elimination of a group of emerging compounds that could be contained in an effluent from a municipal WWTP. For this purpose, 11 micropollutants, most of them pharmaceuticals and pesticides, were selected: acetaminophen, metoprolol, caffeine, antipyrene, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-

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**Table 1**
List of compounds and physico-chemical properties.

| Name | Use | MW, g/mol | p$K_a$ | log $K_{ow}$ | log $D$ (pH 7) | Charge at pH 7 |
|---|---|---|---|---|---|---|
| Acetaminophen | Analgesic, antipyretic | 151.17 | 10.2 | 0.23 | 0.23 | Neutral |
| Metoprolol | β-Blocker | 342.41 | 9.6 | 1.72 | 0.77 | + |
| Caffeine | Psichoactive stimulant | 194.19 | – | −0.45 | −0.45 | Neutral |
| Antipirine | Analgesic, antipyretic | 188.23 | 1.3 | 0.54 | 0.54 | Neutral |
| Sulfamethoxazole | Antibiotic | 253.28 | 1.8; 5.7 | 0.86 | −0.43 | – |
| Flumequine | Antibiotic | 261.25 | 1.3; 6.1 | 1.31 | 0.37 | – |
| Ketorolac | Anti-inflammatory | 255.27 | 4.0 | 2.15 | −0.81 | – |
| Atrazine | Herbicide | 215.69 | 1.7 | 2.52 | 2.52 | Neutral |
| Isoproturon | Herbicide | 206.29 | – | 2.22 | 2.22 | Neutral |
| Hydroxybiphenyl | Biocide | 170.21 | 9.8 | 3.27 | 3.27 | Neutral |
| Diclofenac | Analgesic | 318.14 | 4.3 | 4.29 | 1.62 | – |

hydroxybiphenyl and diclofenac. In the first stage of this work the selected compounds were dissolved in ultrapure (UP) water, and in the second stage in a secondary effluent from a WWTP. Thus, this work differs from previous investigations in which the filtration of a few target compounds dissolved in uncomplicated synthetic model waters or natural waters were studied. The effect of the main operating parameters (transmembrane pressure, tangential velocity, pH, temperature, and nature and molecular weight cut-off (MWCO) of the membranes) on the permeate flux was established, and the retention coefficients of the selected emerging micropollutants, as well as of some global water quality parameters, were evaluated and discussed.

## 2. Materials and methods

### 2.1. Chemicals and membranes

The 11 selected emerging micropollutants mentioned were purchased from Sigma–Aldrich (Germany) and were of 99% purity or higher. Table 1 summarizes the selected compounds and some physico-chemical properties. Values of p$K_a$, log $K_{ow}$ and log $D$ at pH = 7 were calculated by ADME/Tox web software. The solutions used in this study were prepared by simultaneously dissolving them in UP water or in a secondary effluent collected from a municipal WWTP located in Alcalá (Madrid, Spain). This effluent was stored at 4 °C until use, and its main quality parameters are compiled in Table 2.

Several flat sheet commercial membranes provided by GE Osmonics (Florida, USA) were used, all of them with an effective surface area of 28 cm$^2$. They were three UF membranes, denoted GK, PT, and PW with MWCOs of 2000, 5000, and 20,000 Da, respectively; and three NF membranes, denoted CK, DK, and HL, with similar MWCOs, in the range 150–300 Da. Their main properties (material, MWCO and contact angle) are compiled in Table 3. More specifically, the GK membrane was made of thin film composite, with a cross-linked aromatic polyamide top layer; and the PT and PW membranes were of polyethersulfone. These three membranes are hydrophilic, specially the GK membrane with a lower value of contact angle [17]. On the other hand, DK and HL NF membranes were made of thin film composite (polypyperazinamide skin layer on a polyester support), and the CK membrane was of cellulose acetate. According to the determined and published data of contact angles [13,18], the CK membrane is hydrophobic, while DK and HL are hydrophilic.

**Table 2**
Water quality parameters of the selected secondary effluent.

| | |
|---|---|
| COD (mg L$^{-1}$) | 28.8 ± 2.0 |
| UVA$_{254}$ (cm$^{-1}$) | 0.182 ± 0.014 |
| Turbidity (NTU) | 1.0 ± 0.3 |
| pH | 8.2 ± 0.4 |
| Total nitrogen (mg L$^{-1}$) | 11.1 ± 0.4 |
| Total phosphorus (mg L$^{-1}$) | 0.55 ± 0.06 |
| Conductivity (µS cm$^{-1}$) | 701 ± 32 |

### 2.2. Equipment and experimental protocol

The filtration experiments were conducted in the laboratory membrane equipment (CM-CELFA, model P-28) described in detail in a previous publication [19], which operated in cross-flow mode. Basically it was constituted by a 500 cm$^3$ pressurized storage vessel and a pump which fed the solution at the desired flow rates into the device containing the membrane. The transmembrane pressure (TMP) was fixed by pressurizing the storage vessel with nitrogen, the tangential velocity ($v$) was modified by changing the pump flow rate, and the temperature ($T$) was maintained by a recirculated water stream.

Each experiment was performed with a new membrane, which was previously soaked in ultrapure water for 24 h in order to eliminate preservative products. These experiments were conducted in batch concentration mode. A standard operating protocol was followed, which was constituted by three steps: firstly, the new membrane was rinsed with UP water, and the permeate flux ($J_w$) was measured with the aim of determining the membrane pure water permeability (PWP), as will be described later. In a next step, the filtration of the selected emerging micropollutants dissolved in UP water or in the WWTP secondary effluent (300 mL feed water volume with initial concentration of micropollutants of 0.5 mg L$^{-1}$, pH adjusted with phosphate buffer 10 mM) took place. At regular time intervals, the permeate volumes were measured with a balance in order to determine the permeate flux ($J_v$). Simultaneously, samples of the feed, retentate and permeate streams were retired in order to analyze the content of the selected pollutants, as well as the global quality parameters in the WWTP effluent (chemical oxygen demand (COD), absorbance at 254 nm (UVA$_{254}$), total nitrogen (TN), total phosphorus (TP), and turbidity (Turb)). These experiments lasted until a volume reduction factor of 3 was reached, collecting around 200 and 100 mL of permeate and concentrate, respectively. Once the filtration process was finished, at the third step the membrane was again washed with UP water in order to eliminate the cake layer formed on the membrane surface. The PWP was again measured in order to determine the irreversible membrane fouling.

### 2.3. Analytical methods

The analytical methods for the characterization of the WWTP secondary effluent were followed according to the Standard Methods [20]. On the other hand, concentrations of the emerging compounds were determined by HPLC, using a Waters Chromatograph (Waters Alliance 2695) equipped with a 996 Photodiode Array Detector (PAD) and a Phenomenex C18 Column (15 cm × 0.3 cm). A gradient elution of acetonitrile (A) and aqueous solution of formic acid 2.5 × 10$^{-2}$ M (B) was used by varying the percentage of A from 10% to 100% (in volume) over 40 min.

**Table 3**
Properties of target membranes (material, MWCO and pH range provided by manufacturer).

| Membrane | Material | MWCO, Da | pH | Contact angle,° | PWP, $\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$ |
|---|---|---|---|---|---|
| PW | PES | 20,000 | 2–11 | 50 ± 3 | 93.9 ± 5.8 |
| PT | PES | 5000 | 2–11 | 52,8 ± 2 | 21.6 ± 2.7 |
| GK | TF | 2000 | 2–11 | 44 ± 3 | 5.2 ± 0.2 |
| CK | CA | 150–300 | 2–8 | 70 ± 3 | 2.9 ± 0.1 |
| DK | TF | 150–300 | 2–11 | 31 ± 3 | 2.8 ± 0.2 |
| HL | TF | 150–300 | 3–9 | 30 ± 3 | 9.3 ± 0.9 |

**Table 4**
Experimental conditions applied and permeate flux obtained in the filtration of the emerging contaminants dissolved in UP water.

| Expt. | Membrane | TMP, bar | $v$, $\mathrm{m\,s^{-1}}$ | $T$, °C | pH | $J_{vss}$, $\mathrm{L\,h^{-1}\,m^{-2}}$ | $J_{vss}/J_w$ |
|---|---|---|---|---|---|---|---|
| UF-1 | PT | 6 | 2 | 20 | 9 | 86.0 | 0.74 |
| UF-2 | PT | 6 | 2 | 20 | 7 | 126.4 | 0.84 |
| UF-3 | PT | 6 | 2 | 20 | 5 | 82.7 | 0.76 |
| UF-4 | GK | 6 | 2 | 20 | 7 | 24.8 | 0.83 |
| UF-5 | PW | 6 | 2 | 20 | 7 | 423.9 | 0.78 |
| NF-1 | HL | 30 | 2 | 20 | 9 | 218.6 | 0.73 |
| NF-2 | HL | 30 | 2 | 20 | 7 | 242.7 | 0.79 |
| NF-3 | HL | 30 | 2 | 20 | 5 | 209.1 | 0.74 |
| NF-4 | HL | 30 | 2 | 20 | 3 | 238.6 | 0.73 |
| NF-5 | HL | 20 | 2 | 20 | 7 | 177.3 | 0.86 |
| NF-6 | HL | 30 | 2 | 10 | 7 | 162.2 | 0.83 |
| NF-7 | HL | 30 | 1 | 20 | 7 | 228.9 | 0.72 |
| NF-8 | CK | 30 | 2 | 20 | 7 | 72.8 | 0.86 |
| NF-9 | DK | 30 | 2 | 20 | 7 | 85.5 | 0.90 |

The mobile phase flow rate was 0.2 $\mathrm{mL\,min^{-1}}$, and the injection volume was 100 μL. The PAD scanned from 210 to 300 nm, with wavelengths of 220, 250 and 280 nm selected for the quantification of the micropollutants according to their absorption spectra.

## 3. Results and discussion

### 3.1. Membrane characterization: pure water permeability

The first step in the filtration protocol consisted in the filtration of UP water with each new membrane, with the aim of determining the pure water permeate flux ($J_w$). The ratio between this $J_w$ and the TMP of the experiment provided the pure water permeability (PWP), which represents a main characteristic of a membrane. The average values obtained for the different membranes tested are summarized in Table 3. In the UF membranes, it is clearly observed that an increase in the PWP was reached with the increase of the MWCO. Among the NF membranes with similar MWCO, the different PWP experimentally obtained can be attributed to their internal structure, since PWP is a property inherently related to the composition, morphology, and hydrophobicity/hydrophilicity of the membranes. In the present study, the highest PWP value was found for the HL membrane, in a similar way as has been reported in previous works which used this membrane [21].

### 3.2. Filtration of emerging contaminants in UP water

In a following step, the selected emerging micropollutants were simultaneously dissolved in UP water, and filtration experiments were carried out by using the already described UF and NF membranes. The operating variables modified were the MWCO of the membranes, TMP, $v$, $T$, and pH, according to the values summarized in Table 4.

The cumulative permeate volume ($V_P$) was measured continuously through the processing time, and from these $V_P$ values, the permeate fluxes ($J_v$) were obtained by numerical differentiation of the collected mass versus time data. At the same time, the volume reduction factor (VRF) was also evaluated. This factor 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 ($V_R = V_0 - V_P$) [22]:

$$\mathrm{VRF} = \frac{V_0}{V_R} \tag{1}$$

Fig. 1 represents, as an example, the decay of $J_v$ with VRF for some selected experiments of Table 3 (Expts. UF-2, NF-2 and NF-8). As it is observed, $J_v$ decreased slightly with the increase of VRF until an almost constant value was reached, and then remained unalterable for the rest of the experiment. This initial 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. The low decrease in $J_v$ followed by this almost constant value for higher VRF is an indication that low fouling effects are produced in most of the experiments carried out with the selected membranes.

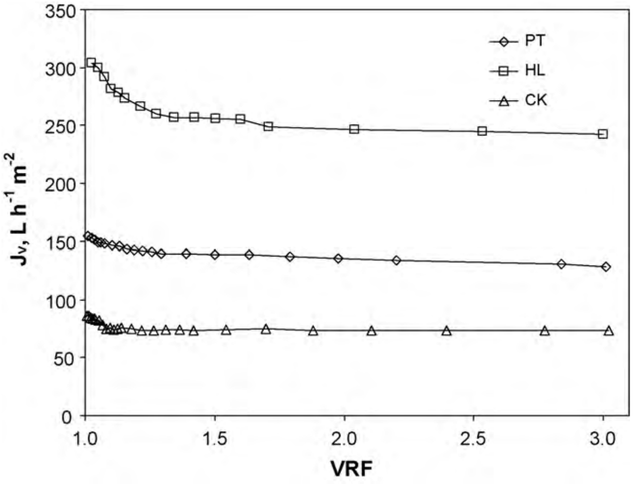

**Fig. 1.** Evolution of the permeate flux with VRF during the filtration of micropollutants dissolved in UP water with the UF PT membrane (Expt. UF-2), and with the NF HL and CK membranes (Expts. NF-2 and NF 8). Experimental conditions detailed in Table 4.

The constant values obtained for the permeate flux are considered as the steady-state permeate fluxes ($J_{\rm vss}$). Thus, in the experiments shown in Fig. 1, the initial permeate flux decreased from 151.0, 305.5, and 85.0 $\rm L\,h^{-1}\,m^{-2}$ to 126.4, 242.7 and 72.8 $\rm L\,h^{-1}\,m^{-2}$ at the steady-state conditions in Expts. UF-2, NF-2, and NF-8, respectively. Table 4 also compiles these steady-state permeate fluxes for all the experiments conducted, as well as the parameter $J_{\rm vss}/J_{\rm w}$. It represents the ratio between the steady-state permeate fluxes for the solutions containing the micropollutants and those corresponding to the filtration of UP water without solutes ($J_{\rm w}$); and it is a measurement of the permeate flux decline ($\mathrm{FD} = 1 - J_{\rm vss}/J_{\rm w}$) due to fouling effects. The similar values of $J_{\rm vss}/J_{\rm w}$ obtained for UF and NF membranes in this case is a consequence of the low fouling promoted in general by the these aqueous solutions with low concentration of solutes.

In the UF experiments compiled in Table 4, a clear influence of MWCO on $J_{\rm vss}$ can be deduced, with an increase of the permeate flux when the MWCO is increased, since a membrane with higher MWCO offers a lower resistance to the solution pass. Thus, the $J_{\rm vss}$ values were 24.8, 126.4 and 423.9 $\rm L\,h^{-1}\,m^{-2}$ for the membranes GK, PT, and PW (MWCOs of 2, 5 and 20 kDa, respectively). However, in the NF process no conclusion could be drawn on the effect of the MWCO, as the three membranes presented similar pore sizes (in the range 150–300 Da). However it is seen a much higher permeate flux for the HL membrane (see Expt. NF-2), while the CK and DK membranes presented lower values (see Expts. NF-8 and NF-9), differences that can be attributed to the different nature of the membranes. Specifically, this sequence agrees with the results previously reported for the PWP of the membranes (see Table 3), with a significant higher value for the HL membrane and similar values for the DK and CK membranes.

Additionally, a direct influence of the TMP on $J_{\rm vss}$ is deduced from the experiments conducted with the HL membrane. Thus, when the TMP was increased from 20 to 30 bar (Expts. NF-5 and NF-2), $J_{\rm vss}$ increased from 177.3 to 242.7 $\rm L\,h^{-1}\,m^{-2}$, although membrane fouling was higher at 30 bar due to the compaction of the cake layer. Similarly, the temperature exerted a positive influence on $J_{\rm vss}$, which increased from 162.2 to 242.7 $\rm L\,h^{-1}\,m^{-2}$ when the temperature was varied from 10 to 20 °C (Expts. NF-6 and NF-2). This result was expected as a consequence of the decrease in the water viscosity and the increase in the diffusivity with the increase in the temperature, with both factors promoting a positive effect on the permeate flux as has been previously reported [23]. Finally, the increase in $v$ (from 1 to 2 $\rm m\,s^{-1}$) also presented an increase in $J_{\rm vss}$, from 228.9 to 242.7 $\rm L\,h^{-1}\,m^{-2}$ (Expts. NF-7 and NF-2), effect that has also been reported for the filtration of some industrial wastewaters [24,25]. This effect could be due to an increase in 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 [26]. Finally, almost no influence is deduced for the pH in both, UF and NF processes. Therefore, pH is not an important parameter from the point of view of permeability.

The retention coefficients constitute a measurement of the efficiency of the membrane, and they can be evaluated by using the expression [27,28]:

$$R = \frac{C_{\rm f} - C_{\rm p}}{C_{\rm f}} \times 100 \qquad (2)$$

where $C_{\rm f}$ and $C_{\rm p}$ are the concentrations of each emerging compound in the feed and permeate solutions, respectively. In the present study, Eq. (2) was applied to the micropollutant concentrations for all the experiments performed at VRF = 3. Table 5 compiles the $R$ values obtained for the 11 selected compounds in all the experiments performed, with a wide range of values as a consequence of the different solute properties that affect the retention: MW, molecular size, p$K_{\rm a}$, log $K_{\rm ow}$, dipole moment, etc.; as well as by the different retention mechanisms, such as adsorption, steric hindrance, electrostatic repulsion, etc.

However, some general trends can be observed: thus, in the UF experiments, it is observed a direct influence of the MWCO of the membranes on $R$, which increased with the decrease in the pore sizes. Then, the highest $R$ values were obtained for the GK membrane with the lowest MWCO (2 kDa), while the lowest values were obtained for the PW membrane with the highest MWCO (20 kDa). In this way, the retentions promoted by the NF membranes are expected to be much larger, as reported by previous researches [27,28]. This effect is confirmed by most of the values summarized in Table 5 for the selected pollutants, with the exception of hydroxybiphenyl, whose $R$ coefficients are quite similar in both, UF and NF processes. Thus, most of these compounds presented retentions above 80% with the NF membranes, although a few of them had lower values (specially acetaminophen), but always higher than in the UF process. Focusing on the NF membranes, the CK membrane provided lower retentions than DK and HL membranes, which can be due to its higher pore size [19]. These results suggest that a NF step would eliminate most of the emerging pollutants from a secondary effluent, being this filtration process an excellent option for its purification before discharge.

The adsorption of micropollutants onto the membrane surface and into the membrane pores was evaluated in order to assess the contribution of this mechanism to the global retention of the solutes by the selected membranes and to establish the retention mechanism for each specific compound. For this purpose, the adsorption percentage (AP) was determined by the expression [27,29]:

$$\mathrm{AP} = \frac{(C_{\rm f}V_{\rm f}) - [(C_{\rm p}V_{\rm p}) + (C_{\rm r}V_{\rm r})]}{C_{\rm f}V_{\rm f}} \times 100 \qquad (3)$$

where $V_{\rm f}$, $V_{\rm p}$, and $V_{\rm r}$ are the feed, permeate and retentate volumes; $C_{\rm f}$, $C_{\rm p}$, and $C_{\rm r}$ are the feed, permeate and retentate concentrations for each micropollutant.

The adsorption percentages of the selected compounds on UF and NF membranes obtained in experiments performed at pH 7 are shown in Fig. 2. The values of AP obtained for the UF membrane GK (MWCO of 2 kDA) and the NF membranes HL, CK and DK are very similar and higher than those observed for the UF membranes PT (MWCO of 5 kDa) and PW (20 MWCO of kDa). Therefore, it results that AP is inversely proportional to the MWCO of UF membranes with similar hydrophilic character (contact angles given in Table 3). One could expect higher values of AP for the hydrophobic NF membrane CK (contact angle of 70°). However, the values of AP are very similar to those of the hydrophilic NF membranes HL and DK, which can be due to the higher pore size of the membrane CK [19] or to the fact that adsorption is not the dominant mechanism for micropollutant retention with NF membranes.

Moreover, the values of AP for each particular micropollutant and UF membrane depicted in Fig. 2A are slightly lower than the values of $R$ shown in Table 5 (Expts. UF-2, UF-4 and UF-5). These results indicate that adsorption is the major retention mechanism for the selected micropollutants with UF membranes. In addition, the contribution of size exclusion should be minor since the MWCOs of the membranes are much higher than the MW of the compounds. The highest retention coefficients in the UF experiments were obtained for hydroxybiphenyl, which is a hydrophobic compound and presents the highest value of log $D$ at pH 7 (3.27, Table 1), which justifies its high adsorption capacity. A second group of compounds is characterized by an intermediate level of retention, specially with the PT membrane: atrazine, isoproturon and diclofenac. These compounds have values of log $D$ at pH 7 around 2, so that can be adsorbed onto the membrane. The remaining compounds are poorly rejected by UF membranes and present values of log $D$ at

**Table 5**
Retention coefficients obtained in the filtration of the emerging contaminants dissolved in UP water (VRF = 3).

| Expt. | $R_{\mathrm{ACET}}$, % | $R_{\mathrm{MET}}$, % | $R_{\mathrm{CAF}}$, % | $R_{\mathrm{ANT}}$, % | $R_{\mathrm{SUL}}$, % | $R_{\mathrm{FLUM}}$, % | $R_{\mathrm{KET}}$, % | $R_{\mathrm{ATR}}$, % | $R_{\mathrm{ISOP}}$, % | $R_{\mathrm{HYD}}$, % | $R_{\mathrm{DIC}}$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| UF-1 | 11.7 | 30.5 | 7.5 | 8.2 | 7.9 | 10.9 | 11.0 | 40.5 | 46.4 | 100.0 | 40.5 |
| UF-2 | 11.3 | 16.9 | 5.7 | 5.8 | 24.7 | 28.4 | 17.6 | 39.0 | 42.0 | 95.4 | 41.6 |
| UF-3 | 11.9 | 15.3 | 8.8 | 11.3 | 25.6 | 40.8 | 29.0 | 38.5 | 43.7 | 95.8 | 75.4 |
| UF-4 | 20.1 | 48.8 | 21.2 | 19.7 | 40.4 | 43.4 | 48.7 | 36.5 | 33.3 | 84.6 | 53.4 |
| UF-5 | 4.7 | 8.1 | 2.1 | 2.3 | 10.2 | 23.0 | 6.1 | 17.9 | 17.4 | 87.9 | 26.5 |
| NF-1 | 23.3 | 100.0 | 85.8 | 88.2 | 97.7 | 93.5 | 95.8 | 91.3 | 83.7 | 96.8 | 96.4 |
| NF-2 | 26.4 | 100.0 | 77.6 | 81.8 | 86.3 | 91.3 | 90.3 | 78.2 | 71.8 | 84.8 | 93.4 |
| NF-3 | 25.0 | 92.4 | 80.9 | 83.8 | 62.9 | 89.6 | 82.4 | 84.6 | 79.2 | 94.1 | 94.9 |
| NF-4 | 21.8 | 100.0 | 77.1 | 82.0 | 48.3 | 80.3 | 68.4 | 76.1 | 77.4 | 82.7 | 98.0 |
| NF-5 | 20.9 | 86.1 | 72.5 | 76.7 | 83.5 | 89.3 | 89.9 | 76.1 | 70.0 | 87.7 | 93.6 |
| NF-6 | 24.5 | 97.9 | 81.2 | 85.5 | 89.3 | 94.4 | 94.3 | 84.2 | 81.4 | 87.4 | 96.7 |
| NF-7 | 32.7 | 97.8 | 72.9 | 77.7 | 85.6 | 90.8 | 89.4 | 79.1 | 69.2 | 87.6 | 93.3 |
| NF-8 | 11.8 | 79.3 | 46.3 | 61.5 | 84.8 | 77.5 | 86.2 | 35.3 | 28.4 | 81.3 | 95.6 |
| NF-9 | 34.3 | 94.4 | 83.7 | 85.4 | 89.7 | 90.5 | 93.6 | 89.8 | 82.7 | 89.3 | 99.8 |

pH 7 below 0.5 (very low adsorption capacity). As a result, there is a good correspondence between retention coefficients and the hydrophobicity of the micropollutants expressed as log *D*.

On the other hand, the values of AP for the NF membranes depicted in Fig. 2B are much lower than the corresponding values of *R* given in Table 5 (Expts. NF-2, NF-8 and NF-9), which confirms that adsorption is not the main mechanism for emerging contaminants retention with NF membranes, except for hydroxybiphenyl, which is efficiently adsorbed on the membranes. The main retention mechanism of the selected micropollutants by NF membranes seems to be size exclusion, since higher retention coefficients were obtained for those compounds with higher molecular weight (metoprolol, diclofenac, flumequine, ketorolac and sulfamethoxazole with MW of 342.41, 318.14, 261.24, 255.27 and 253.28, respectively). Effectively, the retention coefficients obtained in experiments performed at pH 7 with HL, CK and DK membranes were above 90, 80 and 90% respectively (Expts. NF-2, NF-8 and NF-9 in Table 5). The retention of hydroxybiphenyl was also high in spite of its low MW (170.1), which can be explained by the higher adsorption of this hydrophobic compound. The lowest retention coefficient was obtained for acetaminophen, with a MW of only 151.17.

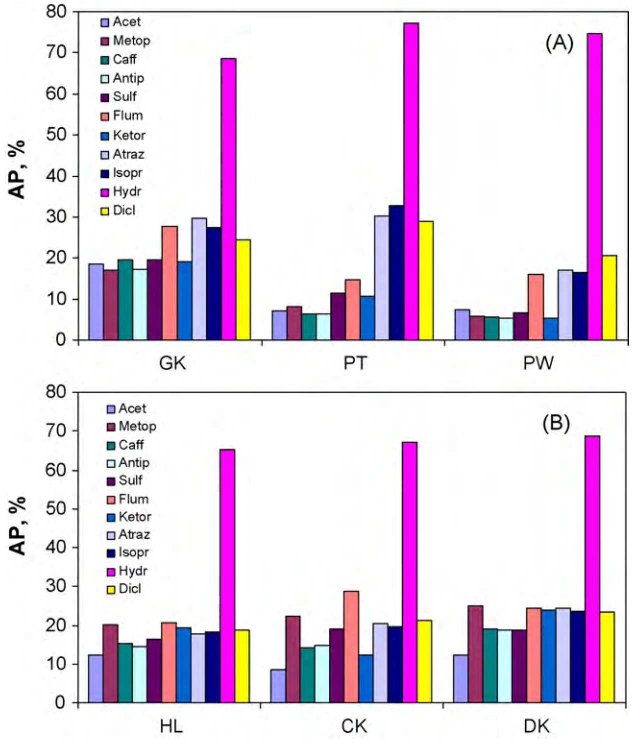

**Fig. 2.** Adsorption percentages (AP) for each selected micropollutant obtained in experiments performed at pH 7 with different (A) UF (Expts. UF-4, UF-2 and UF-5 with GK, PT and PW) and (B) NF (Expts. NF-2, NF-8 and NF-9 with HL, CK and DK) membranes. Experimental conditions detailed in Table 4.

With respect to the influence of the operating variables, a positive effect of the TMP on *R* coefficients is observed for most of the emerging compounds in Table 5 (see Expts. NF-5 and NF-2): these coefficients increased slightly with increasing TMP from 20 to 30 bar, which can be explained by considering that an increase in the TMP leads to an increase of the permeate flux, being this permeate more diluted [30]. On the other hand, the temperature (Expts. NF-6 and NF-2) provided a slight decrease in the *R* coefficients when it was increased from 10 to 20 °C. As it has been previously reported [23], it might be due to a decrease in the water viscosity which increases the permeation flux through the membrane and decreases the retention capacity. Finally, the increase in *v* from 1 to 2 m s$^{-1}$ (Expts. NF-7 and NF-2) provided a slight increase in the *R* coefficients: in effect, the increase in the turbulence at the membrane interface removes part of the accumulated solutes in the cake layer by hydrodynamical forces, leading to a lower concentration of micropollutants on the membrane surface, and thus, higher retention.

Finally, the variation of pH exerted different influence in the UF process with the PT membrane (Expts. UF-1 to UF-3) and in the NF process with the HL membrane (Expts. NF-1 to NF-4). Thus, it can be observed from the values of *R* obtained in Expts. UF-1 to UF-3 (Table 5) that the retention of micropollutants is slightly higher at pH 5 than at pH 9, specially for those compounds which present a negative charge at high pH (sulfamethoxazole, flumequine, ketorolac and diclofenac). At the same time, the values of AP for these compounds decreased at high pH, as can be appreciated in Fig. 3A. These results can be justified if adsorption is the main mechanism responsible for micropollutants retention by UF membranes, being the adsorption of neutral species more favourable [27]. As pH increases, the concentration of negatively charged species also increases, and their hydrophobic character decreases (log *D* decreases versus log $K_{\mathrm{ow}}$ (Table 1)), being their adsorption on the membranes hindered. However, the retention of the selected micropollutant with the NF HL membrane was higher at pH 9 (Table 5, Expts. NF-1 to NF-4), being this positive effect of pH more pronounced for the negatively charged compounds at pH 9 (sulfamethoxazole, flumequine, ketorolac and diclofenac). Similarly to what happened for UF membranes, the adsorption of these compounds decreased with pH (Fig. 3B). These results constitute another indication that adsorption is not the main retention mechanism when NF membranes are used. Instead, and in addition to size exclusion, electrostatic repulsion must contribute efficiently to the retention of negative species at high pH as reported by Yoon

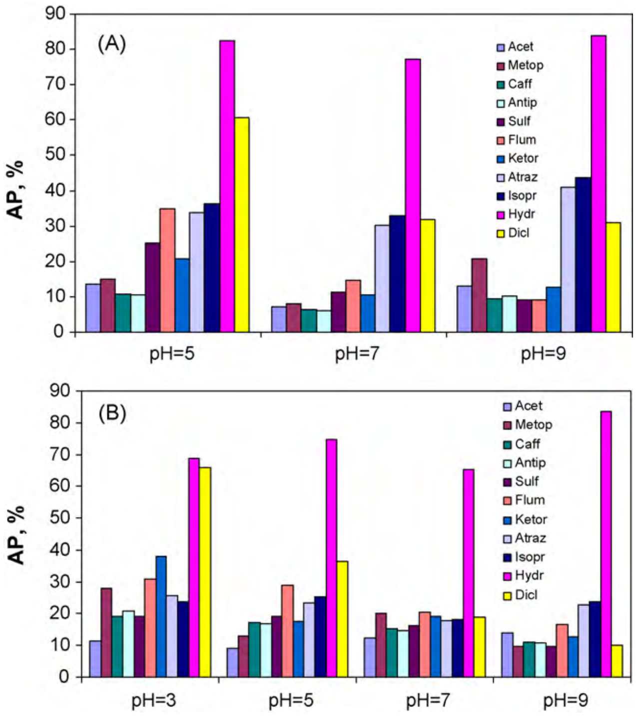

**Fig. 3.** Adsorption percentages (AP) for each selected micropollutant obtained in experiments performed at different pH with (A) the UF PT membrane (Expts. UF-1 to UF-3) and (B) the NF HL membrane (Expts. NF-1 to NF-4). Experimental conditions detailed in Table 4.

et al. [27], while the retention of neutral compounds remains fairly independent on pH.

### 3.3. Filtration of the emerging compounds in the WWTP effluent

A similar set of filtration experiments of the 11 selected emerging compounds was performed when they were present in the WWTP secondary effluent already described, with the same UF and NF membranes, and by modifying again the most important operating conditions: the nature and MWCO of the membranes, TMP, $v$, $T$, and pH. Table 6 compiles these conditions applied in the experiments carried out.

In a similar way as in the experiments performed with the micropollutants dissolved in UP water, $J_v$ decreased with the increase of time, specially in the experiments performed at higher TMP, until an almost constant value was reached at some processing time. This flux decline, which occurred predominantly at the initial processing times, can be attributed to several causes of membrane fouling: cake layer formation, pore blocking, and solutes adsorption onto the membranes. In the present case, the main cause is probably the initial fast pore blocking and adsorption of hydrophobic compounds onto the membrane surface and into the membrane pores, as well as the formation of the cake layer, as reported by Kim et al. [31] for the filtration of wastewater.

**Table 6**
Experimental conditions applied and permeate flux obtained in the filtration of the emerging contaminants dissolved in the secondary effluent.

| Expt. | Memb. | TMP, bar | $v$, m s$^{-1}$ | $T$, °C | pH | $J_{VSS}$, L h$^{-1}$ m$^{-2}$ | $J_{VSS}/J_W$ |
|---|---|---|---|---|---|---|---|
| UF-6 | PT | 6 | 2 | 20 | 9 | 67.3 | 0.49 |
| UF-7 | PT | 6 | 2 | 20 | 7 | 81.9 | 0.56 |
| UF-8 | PT | 6 | 2 | 20 | 5 | 63.1 | 0.52 |
| UF-9 | GK | 6 | 2 | 20 | 7 | 21.7 | 0.68 |
| UF-10 | PW | 6 | 2 | 20 | 7 | 220.0 | 0.38 |
| NF-10 | HL | 30 | 2 | 20 | 9 | 212.7 | 0.81 |
| NF-11 | HL | 30 | 2 | 20 | 7 | 209.4 | 0.78 |
| NF-12 | HL | 30 | 2 | 20 | 5 | 215.2 | 0.72 |
| NF-13 | HL | 30 | 2 | 20 | 3 | 216.9 | 0.79 |
| NF-14 | HL | 20 | 2 | 20 | 7 | 146.0 | 0.81 |
| NF-15 | HL | 30 | 1 | 20 | 7 | 173.4 | 0.70 |
| NF-16 | HL | 30 | 2 | 10 | 7 | 150.8 | 0.75 |
| NF-17 | HL | 30 | 0.5 | 20 | 7 | 160.4 | 0.58 |
| NF-18 | CK | 30 | 2 | 20 | 9 | 56.8 | 0.70 |
| NF-19 | CK | 30 | 2 | 20 | 7 | 63.2 | 0.69 |
| NF-20 | CK | 30 | 2 | 20 | 5 | 62.3 | 0.71 |
| NF-21 | CK | 30 | 2 | 20 | 3 | 58.0 | 0.69 |
| NF-22 | DK | 30 | 2 | 20 | 7 | 65.8 | 0.84 |

Table 6 also shows the steady-state permeate fluxes $J_{VSS}$ as well as the values of the ratio secondary effluent/pure water permeates ($J_{VSS}/J_W$). At a first glance, the flux decrease or fouling was higher (that is, lower values of the ratio $J_{VSS}/J_W$) in UF experiments, which indicates that UF membranes were more sensitive to fouling than NF membranes. Moreover, greater flux decrease values were obtained in the membranes with higher MWCOs: thus, the PW membrane (20 kDa) presented the lowest $J_{VSS}/J_W = 0.38$, equivalent to the highest flux decrease of 62%.

Once again it is difficult to establish the effect of MWCO on $J_{VSS}$ in the NF process due to the similar pore sizes of the membranes (in the range 150–300 Da). Thus, it is obtained a much higher value of $J_{VSS}$ in the HL membrane (209.4 L h$^{-1}$ m$^{-2}$) in comparison to the CK and DK membranes (values of 63.2 and 65.8 L h$^{-1}$ m$^{-2}$), as was previously commented in the NF process of UP water. Additionally, it is also observed that $J_{VSS}$ is affected by the main operating conditions in a similar way as in the experiments with UP water containing the micropollutants, trends that were already discussed in Section 3.2. Thus, positives effects of the TMP, $T$ and $v$ on $J_{VSS}$ are deduced, with increases from 146.0 to 209.4 L h$^{-1}$ m$^{-2}$ for the increase of the TMP from 20 to 30 bar (Expts. NF-14 and NF-11); from 160.4 to 209.4 L h$^{-1}$ m$^{-2}$ for the increase of $v$ from 0.5 to 2 m s$^{-1}$ (Expts. NF-17, NF-15 and NF-11); and from 150.8 to 209.4 L h$^{-1}$ m$^{-2}$ for the increase in T from 10 to 20 °C (Expts. NF-16 and NF-12). Membrane fouling was specially sensitive to the decrease of $v$, since higher tangential velocity reduced the formation of a cake layer. Similar trends were found during the filtration of a secondary effluent without addition of micropollutants [16] and different water matrices [32,33].

The comparison of the values of $J_{VSS}$ and $J_{VSS}/J_W$ in both, the experiments performed with the compounds in UP water and in the WWTP effluent, is presented in Fig. 4, which shows an experiment carried out with each membrane. As this Fig. 4 reveals, the $J_{VSS}$ values reached in the experiments with UP water were in all cases higher than those obtained with the WWTP effluent at the same operating conditions. In addition, the values of $J_{VSS}/J_W$ were lower, and the flux decline was higher in the secondary effluent. Moreover, membrane fouling with respect to UP water was more pronounced for the UF membranes and for the hydrophobic NF CK membrane (higher decreases of $J_{VSS}$ and $J_{VSS}/J_W$ in Fig. 4). However, membrane fouling with UP water or secondary effluent was rather similar for the hydrophilic NF membranes HL and DK. These results are a direct consequence of the larger amount of DOM present in the WWTP effluent (evidenced by the COD content summarized in Table 2) which promotes the adsorption of species onto the membrane as well as pore blocking and the formation of a cake on the membrane surface, specially for hydrophobic membranes with larger pore size.

In this filtration process of the municipal secondary effluent, the effectiveness can be also measured by the retention coefficients referred to some water quality parameters. In general, lower retention coefficients were obtained in the UF process than in the NF process. More specifically, the higher retentions in the UF membranes were deduced for turbidity (69–82%), followed by phosphorus, absorbance at 254 nm, and COD (in the range 38–50%); and nitrogen in a minor extent (11–13%). On the contrary, the higher retentions in the NF process were obtained for phospho-

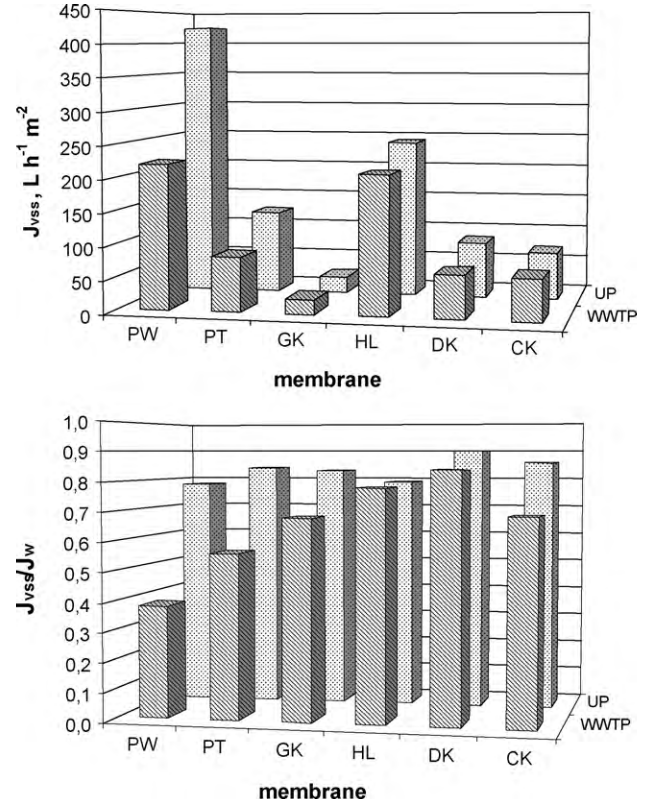

**Fig. 4.** Comparison of values of (A) $J_{vss}$ and (B) $J_{vss}/J_w$ obtained in the filtration of emerging micropollutants dissolved in UP water or in the secondary effluent with the selected UF and NF membranes at pH 7.

rus (higher than 90%); similar retentions for turbidity, absorbance at 254 nm and COD (around 70–90%); and lower values for nitrogen (in the range 30–70%), depending on the operating conditions. These trends are similar to those obtained in a previous work [16], in which the filtration of a secondary effluent from a WWTP without addition of micropollutants was investigated. The main retention mechanisms were adsorption and pore blocking in the UF membranes and in the case of the hydrophobic NF CK membrane; and adsorption, electrostatic repulsion and size exclusion in the case of the hydrophilic NF membranes [16].

The retention coefficients were also determined for the emerging compounds when present in the WWTP effluent, being the values obtained at VRF = 3 detailed in Table 7. Fig. 5 depicts, as an example, the results for some selected experiments that were performed with four of the membranes tested. Thus, most of the emerging compounds presented retentions above 70% for DK and HL membranes, with the exception of acetaminophen; while the CK membrane provided lower retention coefficients. However, lower retention coefficients were obtained with the UF membranes tested (<50% except for hydroxybiphenyl). The influence of the operating variables on the retention coefficients was very similar to that deduced for UP water and discussed previously. Thus, the effect of pH on the retention of negatively charged compounds was negative for UF membranes (due to the decrease of adsorption at high pH) and slightly positive for NF membranes (because of electrostatic repulsion at high pH). The effect of pH on the remaining compounds was not appreciable. In general, these retention coefficients were slightly higher than those obtained in similar experiments performed with UP water. This effect can be explained by the adsorption of hydrophobic compounds on the NOM of the secondary effluent or by the formation of the cake layer, which acts as a second barrier for the retention of micropollutants [34]. In addition, the adsorption percentage was also determined, being the results very similar to those obtained in experiments performed with UP water. Therefore, micropollutants adsorption on NOM compensates the decrease of their adsorption on the membranes due to competition with NOM for membrane active sites.

The permeate fluxes and retention coefficients obtained in the filtration of the WWTP effluent containing the emerging contaminants can be partially explained by measuring the resistances found by the liquid to the pass through the membrane. These resistances (membrane ($R_m$), total fouling ($R_f$), internal fouling ($R_{if}$) and external fouling ($R_{ef}$)) were determined following the procedure described elsewhere [16,35]:

$$R_t = R_m + R_f = R_m + R_{ef} + R_{if} \tag{4}$$

Thus, the fouling resistance was lower than the resistance of the clean membrane, excepting the UF membrane PW with higher MWCO that presented the highest fouling resistance. The values of $R_{if}$ and $R_{ef}$ obtained in the UF experiments were similar, so that the contributions of internal fouling (due to pore blocking and adsorption) and external fouling (mainly due to cake formation) are comparable. However, $R_{ef}$ was higher than $R_{if}$ for the tested NF membranes, which is an indication that the contribution of the cake layer (reduced by physical cleaning) was more important than that of the adsorbed compounds which remained inside the membrane after rinsing with UP water. These results also agree with the fact

**Table 7**
Retention coefficients obtained in the filtration of the emerging contaminants dissolved in secondary effluent (VRF = 3).

| Expt. | $R_{ACET}$, % | $R_{MET}$, % | $R_{CAF}$, % | $R_{ANT}$, % | $R_{SUL}$, % | $R_{FLUM}$, % | $R_{KET}$, % | $R_{ATR}$, % | $R_{ISOP}$, % | $R_{HYD}$, % | $R_{DIC}$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| UF-6 | 14.6 | 4.6 | 7.6 | 10.7 | 28.6 | 10.1 | 26.3 | 44.0 | 49.3 | 100.0 | 41.2 |
| UF-7 | 13.4 | 12.9 | 10.8 | 10.6 | 29.2 | 23.7 | 25.6 | 42.9 | 45.8 | 93.1 | 43.1 |
| UF-8 | 16.1 | 6.6 | 14.5 | 12.5 | 34.5 | 51.3 | 33.6 | 45.8 | 40.0 | 96.4 | 62.6 |
| UF-9 | 11.7 | 21.7 | 16.5 | 17.8 | 33.0 | 29.8 | 35.7 | 39.7 | 31.8 | 82.5 | 39.4 |
| UF-10 | 4.5 | 14.4 | 4.2 | 2.8 | 13.8 | 12.7 | 13.5 | 23.6 | 20.5 | 89.7 | 25.7 |
| NF-10 | 32.4 | 100.0 | 88.2 | 91.8 | 100.0 | 96.9 | 100.0 | 92.0 | 86.6 | 96.3 | 98.5 |
| NF-11 | 26.5 | 100.0 | 82.6 | 84.3 | 94.2 | 92.4 | 93.2 | 88.1 | 78.8 | 95.3 | 93.2 |
| NF-12 | 24.0 | 90.8 | 82.8 | 84.4 | 63.0 | 91.3 | 92.8 | 86.5 | 80.2 | 94.7 | 95.8 |
| NF-13 | 24.6 | 100.0 | 90.1 | 91.3 | 61.9 | 89.9 | 90.4 | 92.1 | 84.1 | 95.2 | 93.7 |
| NF-14 | 27.0 | 100.0 | 84.3 | 88.0 | 95.5 | 97.1 | 100.0 | 91.0 | 84.0 | 97.3 | 96.8 |
| NF-15 | 27.3 | 84.5 | 82.5 | 82.4 | 93.2 | 95.4 | 90.9 | 87.2 | 78.3 | 95.5 | 96.8 |
| NF-16 | 18.5 | 100.0 | 88.6 | 91.7 | 97.1 | 97.9 | 96.1 | 96.5 | 91.5 | 97.8 | 98.3 |
| NF-17 | 23.5 | 97.9 | 69.7 | 76.9 | 88.3 | 94.8 | 89.9 | 78.8 | 71.0 | 95.6 | 96.0 |
| NF-18 | 13.4 | 87.8 | 57.7 | 69.0 | 100.0 | 93.1 | 89.5 | 35.2 | 29.6 | 79.4 | 94.1 |
| NF-19 | 15.8 | 86.1 | 58.0 | 69.7 | 92.5 | 84.6 | 81.2 | 38.9 | 34.5 | 86.6 | 94.0 |
| NF-20 | 16.0 | 86.0 | 57.8 | 66.8 | 46.0 | 66.3 | 69.2 | 44.1 | 29.9 | 84.4 | 83.2 |
| NF-21 | 18.0 | 86.3 | 61.4 | 72.9 | 42.3 | 62.3 | 60.0 | 44.5 | 33.7 | 83.8 | 97.6 |
| NF-22 | 39.6 | 100.0 | 89.9 | 91.2 | 97.2 | 96.3 | 98.0 | 95.0 | 87.9 | 86.0 | 100.0 |

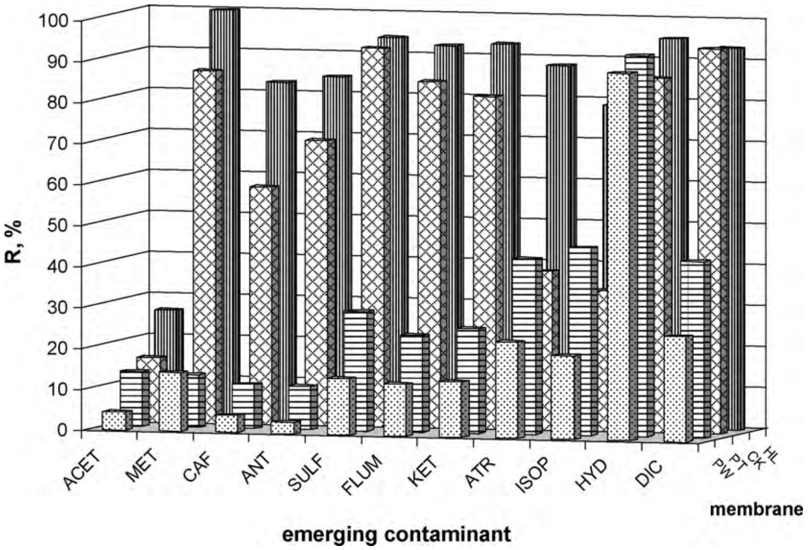

**Fig. 5.** Influence of the MWCO and nature of some UF and NF membranes on the retention of emerging compounds at VRF = 3 (Expts. UF-7, UF-10, NF-11 and NF-19 in Table 6).

that adsorption is the main mechanism for membrane fouling and micropollutants retention by UF filtration membranes. However, other retention mechanisms are important in the case of NF membranes, such as size exclusion and electrostatic repulsion at high pH.

## 4. Conclusions

From the results obtained in the UF and NF experiments of 11 emerging contaminants dissolved in ultrapure water or in a secondary effluent from a WWTP, it was found that flux decline, and therefore membrane fouling, were higher for UF membranes, especially when the secondary effluent was used. This permeate flux decline could be explained by the resistances in model series, being fouling resistances elevated in membranes with higher MWCO. In addition, while the contribution of both internal and external fouling were similar in the selected UF membranes, only external fouling was important in the filtration with NF membranes.

The retention of the selected micropollutants was above 70% for DK and HL membranes, with the exception of acetaminophen; while the CK membrane provided lower retention coefficients. However, lower retention was obtained with the UF membranes tested (<50% except for hydroxybiphenyl). The effect of pH on the retention of negatively charged compounds was negative for UF membranes (due to the decrease of adsorption at high pH) and slightly positive for NF membranes (because of electrostatic repulsion at high pH). While adsorption is the main retention mechanism for UF membranes, size exclusion and electrostatic repulsion of negative species at high pH are responsible for micropollutant retention by NF membranes.

Considering the main water quality parameters of the permeate stream, it can be concluded that UF led to moderate retentions, while NF promoted higher retentions of the organic and inorganic matter present in the secondary effluent. Moreover, taking into account the permeate flux, PT and HL membranes, among UF and NF membranes respectively, provided the best results for the retention of micropollutants at high permeate fluxes. Therefore, these membranes constitute promising options for the treatment of secondary effluents from municipal WWTP, with the aim of obtaining a permeate with good physico-chemical quality, which could be reused in several applications, such as irrigation, recharge of aquifers, etc.

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