Nanofiltration processes applied to the removal of phenyl-ureas in natural waters

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ABSTRACT

Four phenyl-urea herbicides (linuron, diuron, chlortoluron and isoproturon) dissolved in a commercial mineral water and in reservoir water were subjected to nanofiltration (NF) processes in cross-flow laboratory equipment with recycling of the retentate stream. Three NF membranes of different nature, with molecual weigth cut-off (MWCO) in the range 150–300 Da, were used. The hydraulic permeabilities of the membranes were determined from filtration experiments of ultra-pure (UP) water. In the NF of the synthetic waters, the permeate fluxes were evaluated, the influence of the main operating conditions (transmembrane pressure, temperature, and MWCO of the membranes) on the steady-state permeate fluxes was established, and the different resistances found in the system, which are responsible of the flux declines, were deduced. The retention coefficients for each herbicide were also evaluated and discussed in view of the nature and characteristics of herbicides and membranes. Finally, the herbicides mass adsorbed on the membranes were also determined and the contribution of the adsorption mechanism to the global retention is pointed out.

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1. Introduction

A wide variety of studies can be found in the literature about the use of ultrafiltration (UF) and nanofiltration (NF) membranes for the removal of conventional micropollutants (pesticides, pharmaceuticals, endocrine disrupting compounds, etc.) for the production of drinking water [1–4]. In general these pressure-driven membrane processes present different advantages, such as the high quality of the final permeate, the low requirements in temperature and energy, the absence of chemicals, and their combination with supplementary separation processes. However, membrane fouling constitutes the main disadvantage of these techniques. This problem leads to a reduction of the permeate flux, and has been associated with the organic matter content of the water under treatment. Several factors seems to contribute to this flux decline: the concentration polarization due to the accumulation of solutes in a layer, the formation of a solid cake onto the membrane surface, the deposition of molecules in the membrane pores with the subsequent pores blocking, and the very important adsorption of solutes on the membrane.

Particularly NF has higher rejection efficiencies for small organics than UF processes, and have been studied in recent times as potentially useful for pesticides removal, considering the fact that molecular weights of most pesticides are more than 200 Da [1,5].

However, there is still a long list of pesticides with a lack of data for their effective separation by using membranes, including the phenyl-urea herbicides. Although results on the retention of diuron and isoproturon by NF membranes have been reported previously [6], the filtration of linuron and chlortoluron has not been reported yet. In addition, studies on the effect of fouling of NF membranes on permeate flux decline and simultaneous micropollutants retention are rather limited. These phenyl-urea herbicides are reported to be among the most widely used herbicides in agriculture today [7], because of their multiple applications. As a consequence, they have been detected in wastewater effluents and raw drinking source waters around the world at concentrations of micrograms per liter [8]. Due to the potential risks to humans and wildlife even at those low concentrations, the removal of phenyl-ureas constitutes an important issue in the water purification industry, which tries to protect the environment in general, and to remove refractory organics in particular, such as these herbicides.

With these aspects in mind, the present research was designed with the final goal of examining the performance of several NF membranes to retain four selected phenyl-urea herbicides from waters: linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), chlortoluron (3-(3-chloro-4-methylphenyl)-1,1-dimethylurea), and isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea). These micropollutants were dissolved in two water systems (a commercial mineral water, and a surface water from a public reservoir) and were subjected to cross-flow filtration experiments, with several objectives being pursued: the study of the evolution of the

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permeate flux with filtration time and volume retention factors; the establishment of the effect of several operating parameters (transmembrane pressure, initial herbicide concentrations, and types of membranes used) on the steady-state permeate flux; the evaluation of the partial contribution of the different membrane resistances; and the determination of retention coefficients and adsorbed mass for each herbicide, including the proposition of the main retention mechanisms. Finally, the additional presence of humic acids and calcium ions was also investigated, since these compounds might decrease the permeate flux and therefore affect the retention coefficients.

2. Materials and methods

2.1. Herbicides, water systems and NF membranes

Table 1 provides the molecular structures and molecular weights of the selected phenyl-ureas, as well as their permanent dipole moment and $\log K_{ow}$ values. The permanent dipole moment is a measurement of the polarity of a molecule, and they were calculated by using the computer program Hyperchem, with the following values obtained: 4.76, 5.87, 4.92 and 3.31 Debye for linuron, diuron, chlortoluron and isoproturon, respectively. On the other hand, the $\log K_{ow}$ parameter indicates the hydrophobic/hydrophilic character of a substance, and was determined by using the ACD/ChemSketch software, since some discrepancies were found in the literature [1,4,9] for the values of $\log K_{ow}$, specially for isoproturon. The values obtained were 3.20, 2.78, 2.35 and 2.32 for linuron, diuron, chlortoluron and isoproturon respectively. As $\log K_{ow} > 2$, the herbicides can be considered as hydrophobic, moderately soluble in water and therefore weakly polar compounds.

The herbicides were dissolved in two water systems: a mineral water (denoted M) from the commercial brand "Los Riscos" (Alburquerque, Spain) and a surface water (denoted R) which was collected from a public reservoir ("Peña del Aguila" reservoir, in the Extremadura Community, southwest of Spain). The absorbances at 254 nm of these waters were 0.004, and 0.125; the DOC content was 1.2, and 6.7 mg L^{-1}, and the alkalinity was 1.2, and 0.47×10^{-3} M in HCO$_3^-$ for the mineral and the reservoir water, respectively. UV

absorbances and DOC content are parameters that provide an indication of the natural organic matter (NOM) content in both waters systems. Humic acids (HA, Fluka) and calcium chloride were added in some experiments as NOM and calcium ions source.
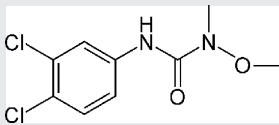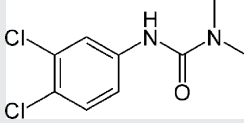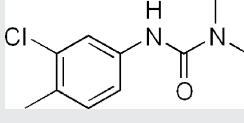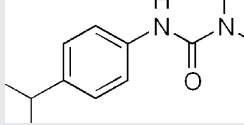
The membranes used in this study (denoted DK, DL and CK) were commercial flat-sheet membranes provided by GE Osmonics, Inc. (FL, USA), with an effective surface area of 28 cm^2. According to the manufacturer, they had similar MWCO, in the range 150–300 Da. Further specific measurements made by Petrinic et al. [10] established values of 230 and 340 Da for the DK and DL membranes, respectively. These membranes were constituted by different materials: thus, the DK and DL were made of thin film composite (polypyperazinamide skin layer on a polyester support), and were negatively charged because of their active nanopolymer layer; and the CK membrane was made of cellulose acetate polymers and also, negatively charged. On the other hand, the CK membrane presented a hydrophobic character (contact angle of 59°); while both, the DK and DL membranes, were hydrophilic (contact angle of 41°C and 30.7°C, respectively) [11,12].

2.2. Experimental procedures and analysis

The laboratory cross-flow membrane filtration unit (supplied by CM-CELFA Membrantechnik AG, model P-28^{TM}, Seewen, Switzerland) that was described in detail in a previous study [12] was used in this work. It basically consists of a 500 mL pressurized storage vessel with a device containing the membrane. The transmembrane pressure (TMP) control in these NF experiments was carried out by feeding nitrogen gas to the head of the storage vessel, and the temperature of the feed solution was kept constant at the desired value by recirculating a water stream from a thermostated bath around the storage vessel. The tangential velocity was kept constant at 2 m s^{-1}, and the experiments were performed at the natural pH of the waters (8.0 ± 0.1). A new membrane was used for each experiment.

A batch concentration mode procedure was selected to carry out all the NF experiments, with the permeate stream collected separately, and the retentate stream recycled to the feed tank. It followed a standard protocol consisting of three steps: firstly, the

Table 1
Properties of the selected herbicides.

Herbicide	Chemical structure	Molecular formula	Molecular weight (Da)	Dipole moment (Debye)	$\log K_{ow}$[a]
Linuron		$C_9H_{10}Cl_2N_2O_2$	249.10	4.76	3.20
Diuron		$C_9H_{10}Cl_2N_2O$	233.10	5.87	2.78
Chlortoluron		$C_{10}H_{13}ClN_2O$	212.68	4.92	2.35
Isoproturon		$C_{12}H_{18}N_2O$	206.29	3.31	2.32

[a] Determined by the software ACD ChemSketch.

water permeate flux (J_w) was measured in the filtration process of ultrapure (UP) water, and these J_w values were used to determine the membrane hydraulic permeability (L_p). Secondly, the phenyl-urea herbicides NF experiments were performed, by filling the storage tank with the solution containing the mixture of herbicides (300 mL) at the desired initial concentrations (5–10 μM). At regular times the collected permeate volume (V_P) was weighted with a Mettler balance, and the permeate flux (J_v) of the solution was determined. Samples of the feed, retentate and permeate streams were simultaneously collected and the herbicides concentrations were analysed in these samples. These experiments lasted until a volume reduction factor of 4 was reached, collecting around 225 and 75 mL of permeate and concentrate, respectively. Following the herbicide filtration experiments, in a third step the membrane was again rinsed with UP water in order to eliminate the possible concentration polarization and cake layer formed, which are the main causes of the reversible membrane fouling. Then, the pure water permeate flux was again measured, and thus, the irreversible membrane fouling was determined.

With respect to the determination of the membrane hydraulic permeability, as the TMP was varied in the DK membrane, the resulting J_w values were plotted against the applied pressures and a linear relationship was found: the membrane permeability was determined from the slope of the resulting straight line. After regression analysis, a value of 3.5 L h⁻¹ m⁻² bar⁻¹ was deduced at 20 °C. However, as the filtration experiments with the DL and CK membranes were carried out at a constant TMP pressure, the L_p was the resulting ratio between J_w and the TMP applied, and the values obtained were 3.8 and 2.8 L h⁻¹ m⁻² bar⁻¹ for DL and CK membranes, respectively. The three membranes present similar values, as could be expected, due to their similar MWCO, and the differences can be attributed to their internal structures. Thus, the CK membrane exhibited relatively hydrophobic surface and slightly lower pure water permeability in comparison to the DK and DL membranes. On the other hand, the higher value of L_p in the DL membrane can be explained by its slightly higher MWCO previously noted (230 and 340 Da for DK and DL membranes respectively) [10]. In effect, it is expected that larger pore sizes or MWCO led to higher pure water fluxes. Finally, since the temperature effect

on the filtration process was investigated with the DK membrane, its hydraulic permeability was also measured at two other temperatures. The values of L_p obtained at 10 and 30 °C were 2.9 and 4.5 L h⁻¹ m⁻² bar⁻¹, respectively. From the results at the three temperatures selected, it is concluded that a temperature increase leads to higher pure water permeability, which is due to an increase of the mass transfer coefficient.

The concentration of the selected herbicides in the collected samples was determined by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column, following the procedure described previously [13]. In these analysis, the elution flow rate was 1 mL min⁻¹, the detection was carried out at 248 nm and the mobile phase was a mixture of methanol and 10⁻² M phosphoric acid aqueous solution (45:55 v/v, methanol:water). Absorbance at 254 nm ($UV_{254 nm}$) was measured with a Unican Helios β spectrophotometer. Dissolved organic carbon (DOC) was determined by an IO Analytical total organic carbon analyzer, based on persulfate oxidation method. The chemical oxygen demand (COD) was measured by using the standard methods [14].

3. Results and discussion

3.1. Permeate flux and analysis of resistances

The filtration of the selected phenyl-ureas dissolved in the mineral and reservoir waters was carried out by using the NF membranes previously described, and by varying the following operating conditions: different types of membrane, TMP, temperature, and initial concentration of herbicides. Table 2 summarizes the experiments performed and details the specific values applied for these operating conditions.

The permeate fluxes (J_w when pure water was filtrated, or J_v when the herbicides solutions were used) were evaluated from the permeate streams collected at regular times during each experiment, by measuring their weights with an electronic balance. The cumulative weights were converted to cumulative permeate volumes (V_p), and the permeate fluxes were determined by the
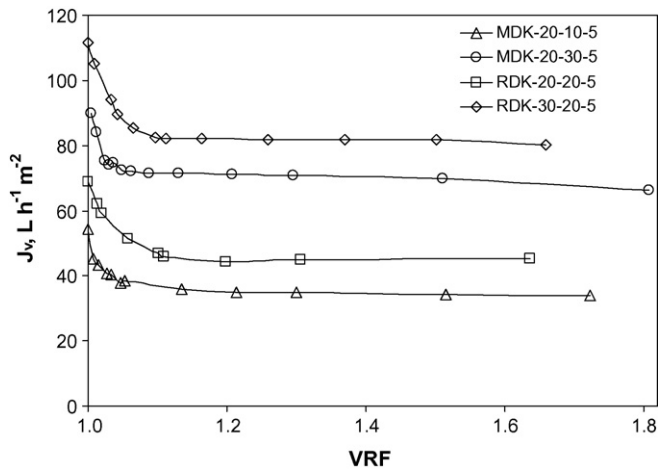
Table 2
Experimental conditions applied in the NF of phenyl-ureas dissolved in mineral (M) and reservoir (R) waters and results obtained for the steady-state permeate flux and the flux reduction.

Experiment	Membrane	TMP (bar)	T (°C)	$[P]_0$ (μM)	J_{vss} (L h⁻¹ m⁻²)	J_{vss}/J_w
MDK-10-20-5	DK	10	20	5	23.8	0.72
MDK-20-20-5	DK	20	20	5	49.6	0.70
MDK-30-20-5	DK	30	20	5	81.1	0.75
MDK-20-10-5	DK	20	10	5	35.1	0.59
MDK-20-30-5	DK	20	30	5	72.4	0.78
MDK-20-20-10	DK	20	20	10	49.9	0.74
MCK-20-20-5	CK	20	20	5	42.6	0.73
MDL-20-20-5	DL	20	20	5	55.7	0.74
RDK-10-20-5	DK	10	20	5	23.1	0.70
RDK-20-20-5	DK	20	20	5	48.9	0.70
RDK-30-20-5	DK	30	20	5	81.4	0.71
RDK-20-10-5	DK	20	10	5	34.1	0.57
RDK-20-30-5	DK	20	30	5	71.7	0.76
RDK-20-20-10	DK	20	20	10	46.5	0.71
RCK-20-20-5	CK	20	20	5	40.7	0.71
RDL-20-20-5	DL	20	20	5	54.9	0.73
RDK-20-20-5-Ca[a]	DK	20	20	5	47.1	0.68
RDK-20-20-5-HA[b]	DK	20	20	5	49.5	0.69
RDK-20-20-5-Ca-HA[c]	DK	20	20	5	45.8	0.63

[a] Addition of 100 mg L⁻¹ Ca²⁺.

[b] Addition of 5 mg L⁻¹ HA.

[c] Addition of 100 mg L⁻¹ Ca²⁺ and 5 mg L⁻¹ HA.

Fig. 1. Evolution of the permeate flux with the VRF for some selected experiments. Experimental conditions detailed in Table 2.

Fig. 2. Steady-state permeate flux obtained for the different membranes tested. Experiments MDK-20-20-5, MCK-20-20-5 and MDL-20-20-5; and RDK-20-20-5, RCK-20-20-5 and RDL-20-20-5.

equation:

$$J_W \text{ or } J_v = \frac{\Delta V_p}{\Delta t A} \tag{1}$$

where ΔV_p is the accumulated permeate volume during the time difference Δt, and A is the membrane area. On the other hand, the volume reduction factor (VRF), was calculated by using the equation:

$$\text{VRF} = \frac{V_0}{V_R} \tag{2}$$

This equation takes into account the ratio between the initial feed volume (V_0) and the volume remaining in the storage vessel ($V_R = V_0 - V_p$), V_p being the already mentioned cumulative permeate volume.

The evolution of J_v with VRF is represented in Fig. 1 for some selected experiments carried out with the DK membrane: it is observed that J_v initially decreases with the increase of VRF, and later, remained constant for the rest of the experiment. This initial decline in J_v is a direct consequence of the fouling effect that occurs in the membrane, which in the present case, focused on the NF of model compounds dissolved in natural waters, is low to moderate. However, the fouling effect is more significant in the NF of industrial wastewaters [12,15,16] with much higher pollutant contents. As similar decay curves of J_v were obtained for the remaining experiments not shown in Fig. 1, with constant permeate fluxes reached for VRF in the range 1.0–1.2, VRF = 1.1 was selected as the average value that provided the steady-state permeate flux (J_{vss}) for the NF of the phenyl-urea solutions in the mineral and reservoir waters; and the results obtained for J_{vss} are showed in Table 2. In addition, Table 2 also includes the values of J_{vss}/J_w: this parameter reflects the ratio between the permeate fluxes of the herbicide solutions and that of pure water, and constitutes a measurement of the flux decline. Its value must be lower than 1, due to the fouling in the membrane by the presence of the inorganic and organic matrix of the selected waters and the pollutants (the herbicides in the present case).

The influence of the TMP on J_{vss} for the two selected water systems can be deduced from the results with the DK membrane summarized in Table 2. As observed, an increase in the TMP had a positive effect on the permeate flux, with an almost linear variation, as it could be expected. The same effect has been recently reported by Ahmad et al. [17] for the NF of dimethoate and atrazine and by using, among other membranes, the same DK membrane. As it has been pointed out [18], this linear relationship is a characteristic of
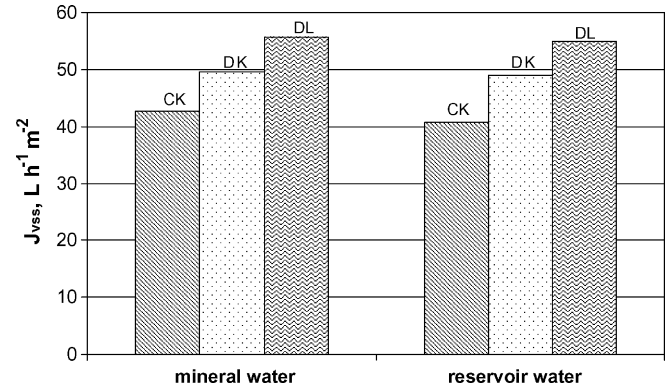
less severe fouling phenomena and usually occurs in membranes with lower MWCO, especially for values of MWCO <40 kDa. This condition is widely fulfilled in the NF membranes used in this work, with much lower MWCO (150–300 Da). However, the flux decline, measured as the ratio J_{vss}/J_w, was independent on the TMP.

On the other hand, as Fig. 2 shows, it was also obtained that for a given TMP and temperature (20 bar and 20 °C), the DL membrane provided higher permeate fluxes than the DK and CK membranes for both water types. This result is attributed to the different nature of the membranes detailed in Section 2.1, and agrees with the previously reported values of L_p: in effect, the highest permeability corresponded to the DL membrane, intermediate for the DK membrane and the lowest for the CK membrane (3.8, 3.5 and 2.8 L h^{-1} m^{-2} bar^{-1}, respectively). From the values of J_{vss}/J_w detailed in Table 2, it is deduced that the flux decline was similar for the three selected membranes (25–30%).

As Table 2 and Fig. 2 reveal, the J_{vss} values reached for the mineral water were slightly higher than those of the surface water in experiments conducted at the same operating conditions. As a consequence, the values of J_{vss}/J_w were slightly lower in the reservoir water. This decrease in the permeate flux is a consequence of the larger amount of DOM present in the reservoir water (evidenced by UV absorbance and DOC content, see Section 2.1) which induces a larger adsorption of species onto the membrane as well as pore blocking with the formation of a cake on the membrane surface. Therefore, the NF of reservoir water through membranes is a more difficult process with slightly higher resistances, thus resulting in lower permeate fluxes.

The increase of the temperature from 10 to 30 °C exerted an increase in the J_{vss} in experiments with the DK membrane in both water systems (Table 2: Expts. MDK-20-10-5, MDK-20-20-5 and MDK-20-30-5; and RDK-20-10-5, RDK-20-20-5 and RDK-20-30-5). As it is expected, an increase in the temperature promotes a decrease in the viscosity and an increase in the diffusivity of the solution, and both variables cause a positive effect on the permeate flux [19]. In addition, membrane fouling was more severe at lower temperature as can be deduced from the values of J_{vss}/J_w shown in Table 2. With the J_{vss} values obtained at different temperatures an Arrhenius plot was performed, and after regression analysis (with T in K and J_{vss} in L h^{-1} m^{-2}), the following expressions were deduced:

$$J_{vss} = 1.99 \times 10^6 \exp\left(\frac{-3101}{T}\right) \quad (R^2 = 0.997) \text{ for mineral water} \tag{3}$$

$$J_{vss} = 2.60 \times 10^6 \exp\left(\frac{-3184}{T}\right) \quad (R^2 = 0.998) \text{ for reservoir water}$$
$$(4)$$

Finally, the effect of the initial herbicide concentrations on the J_{vss} was also studied in the NF process with the DK membrane (Expts. MDK-20-20-5 and MDK-20-20-10 for the mineral water, with initial concentrations of the four herbicides of 5 and 10 μM; and similarly in Expts. RDK-20-20-5 and RDK-20-20-10 for the reservoir water). As can be deduced from the values shown in Table 2, the increase in this initial concentrations resulted in similar permeate flux values, and the flux decline J_{vss}/J_w remained almost constant. Ahmad et al. [17] also observed very little effect on the permeate flux obtained in the dimethoate and atrazine NF process when increasing their initial concentrations. Therefore, the effect of micropollutant concentration can be excluded from consideration when the flux performance is investigated.

As pointed out above, the decrease in the permeate flux is a consequence of the adsorption of species (NOM and ions onto the membrane) as well as pore blocking and formation of a cake layer on the membrane surface. Consequently, a decrease of the effective pore size is caused, which leads to a decrease of the water flux. In order to investigate the effect of the additional presence of NOM and ions on the water flux, some experiments were performed by adding an extra amount of NOM (humic acids) and calcium ions to the reservoir water (Expts. RDK-20-20-5-Ca, RDK-20-20-5-HA and RDK-20-20-5-Ca-HA in Table 2). It can be appreciated that the additional presence of both NOM and calcium ions led to a further decrease of the water flux (compared to Expt. RDK-20-20-5 carried out under similar experimental conditions) as well as to a decrease of the ratio J_{vss}/J_w. These results can be explained by the adsorption of NOM and ions inside the membrane pores [20]. The extent of the membrane fouling was more important in the presence of both humic acids and calcium ions, which could be due to the formation of calcium complexes of humic acids, which are characterized by a high hydrophobicity and a low solubility [1]. These results can also be explained by pore blocking, caused by molecules with a size similar to the size of the pores. Such a molecule can block the membrane pore efficiently so that the pore becomes unavailable for further filtration [6].

The permeate flux decline previously pointed out is a consequence of the resistances found by a solution during its NF process.

Then, this decline can be analysed by means of the resistances in series model. In effect, the total hydraulic resistance R_t found by the solution can be determined from the permeate flux values, by applying the general Darcy's law [21,22]:

$$R_t = \frac{\text{TMP}}{\mu J_v} \tag{5}$$

where μ is the viscosity of the herbicide solutions and TMP the transmembrane pressure of each experiment. This total resistance R_t is the result of the contribution of different resistances in series:

$$R_t = R_m + R_f = R_m + R_{ef} + R_{if} \tag{6}$$

where R_m is the inherent hydraulic resistance of a clean membrane, and R_f is the fouling resistance, resulting from the contributions of the external and internal fouling resistances. The external fouling resistance (R_{ef}) is due to concentration polarization and deposition of solids (cake layer) on the membrane surface. As was described in Section 2.2, this external fouling can be removed by cleaning the membrane with UP water, after each filtration experiment. The internal fouling resistance (R_{if}) is due to pore blocking and adsorption of materials onto the membrane surface and pores, and therefore, it cannot be removed by water cleaning [21].

In this work, all these resistances were determined from the permeate flux data obtained according to the protocol previously explained in Section 2.2: thus, R_m was calculated by using Eq. (5) in the initial filtration experiments of UP water performed with each new membrane. In that case, the viscosity corresponded to that of the pure water (μ_w), and J_v was the permeate flux of this pure water (J_w). Later, R_t was determined in the same way, by applying Eq. (5) to the NF filtration experiments of the solutions containing the phenyl-urea herbicides dissolved in both, mineral and reservoir waters. According to Eq. (6), the difference between both resistances, R_t and R_m, provided the R_f values. Finally, the R_{if} resistance was evaluated from the permeate fluxes determined in the final filtration step with UP water, once the membranes had been washed in order to eliminate the concentration polarization and cake layer.

Table 3 summarizes the results obtained for these resistances, and several trends can be deduced from these results. Thus, when comparing the experiments performed at 20 bar and 20 °C, the lowest R_t values corresponded to the DL membrane, with values of 12.9 and 13.1 × 10^{13} m^{-1} for mineral and reservoir waters, respec-

Table 3
Values obtained for the resistances in the NF of phenyl-urea solutions.

Experiment	$R_t \times 10^{-13}$ (m^{-1})	$R_m \times 10^{-13}$ (m^{-1})	$R_f \times 10^{-13}$ (m^{-1})	$R_{if} \times 10^{-13}$ (m^{-1})	$R_{ef} \times 10^{-13}$ (m^{-1})	R_f/R_t (%)
MDK-10-20-5	15.1	10.9	4.2	1.2	3.0	28.0
MDK-20-20-5	14.5	10.2	4.3	1.0	3.3	29.8
MDK-30-20-5	13.3	10.1	3.2	1.2	2.0	24.2
MDK-20-10-5	20.5	12.1	8.4	3.0	5.4	41.0
MDK-20-30-5	9.9	7.7	2.2	0.5	1.7	22.1
MDK-20-20-10	14.4	10.7	3.7	1.5	2.2	25.9
MCK-20-20-5	16.9	12.5	4.4	2.4	2.0	26.3
MDL-20-20-5	12.9	9.5	3.4	1.2	2.2	26.3
RDK-10-20-5	15.6	10.9	4.7	1.1	3.6	30.1
RDK-20-20-5	14.7	10.3	4.4	1.1	3.3	30.0
RDK-30-20-5	13.3	9.5	3.8	1.1	2.7	28.4
RDK-20-10-5	21.1	12.1	9.0	2.6	6.4	42.8
RDK-20-30-5	10.0	7.9	2.1	0.7	1.4	20.9
RDK-20-20-10	15.5	11.1	4.4	1.3	3.1	28.6
RCK-20-20-5	17.7	10.8	6.9	2.8	4.0	39.1
RDL-20-20-5	13.1	9.6	3.5	0.9	2.6	26.5
RDK-20-20-5-Ca[a]	15.3	10.5	4.8	2.4	2.4	31.5
RDK-20-20-5-HA[b]	14.6	10.1	4.5	2.1	2.4	30.8
RDK-20-20-5-Ca-HA[c]	15.7	10.0	5.7	3.0	2.7	36.5

[a] Addition of 100 mg L^{-1} Ca^{2+}.

[b] Addition of 5 mg L^{-1} HA.

[c] Addition of 100 mg L^{-1} Ca^{2+} and 5 mg L^{-1} HA.

Experiment	R_L (%)	R_D (%)	R_C (%)	R_I (%)
MDK-10-20-5	72.9	57.2	63.6	83.2
MDK-20-20-5	74.5	60.2	68.8	84.4
MDK-30-20-5	82.3	74.4	81.6	91.7
MDK-20-10-5	85.5	76.8	82.1	91.4
MDK-20-30-5	66.3	49.0	58.5	79.1
MDK-20-20-10	80.4	70.6	77.1	90.3
MCK-20-20-5	71.2	38.6	24.3	23.0
MDL-20-20-5	59.9	42.6	47.5	68.9
RDK-10-20-5	74.9	63.0	69.0	85.2
RDK-20-20-5	83.6	75.1	80.8	90.8
RDK-30-20-5	85.2	78.6	83.8	91.9
RDK-20-10-5	87.4	83.9	85.8	91.4
RDK-20-30-5	76.1	66.9	73.6	82.3
RDK-20-20-10	85.1	74.8	80.3	92.5
RCK-20-20-5	79.9	38.7	25.6	25.0
RDL-20-20-5	65.3	46.4	49.4	68.4
RDK-20-20-5-Ca[a]	84.1	75.4	78.7	89.3
RDK-20-20-5-HA[b]	86.0	77.3	81.0	90.7
RDK-20-20-5-Ca-HA[c]	86.5	77.4	81.1	91.8

tively, which again is in accordance with the L_p and J_{vss} values: in effect, this membrane reached the highest permeability and permeate flux values as a consequence of this lower global resistance. On the contrary, the CK and DK membranes presented higher R_t resistances (the highest values for the CK), and consequently, they reached lower L_p and J_{vss} values. It is also observed for the three membranes that the partial contribution of the fouling resistance (R_f) to the total resistance R_t was smaller than the contribution of the inherent resistance of the clean membrane R_m, with most values for ($R_f/(R_f + R_m) \times 100$) in the range 20–43%, depending on the operating conditions. These smaller values of R_f confirm that the membrane fouling is low to moderate in these experiments performed with natural waters; and then, it can be concluded, that the total resistance was mainly due to the contribution of the inherent membrane resistance R_m. In contrast, UF and NF of industrial wastewaters revealed that the partial contribution of R_f to the total resistance R_t is much higher than the contribution of R_m, due to greater fouling effects on the membranes [15,22].

By considering the effect of the operating variables, it can be seen that the different resistances to the filtration of the herbicide solutions (R_t and R_f) decreased with the increase in the TMP for both waters, as could be expected: an increase in the TMP promotes an increase in the driving force through the membrane, and consequently, a decrease in the resistances to the filtration process. Similarly, the increase in the temperature also provides a decrease in the resistances, due to an improvement in the permeate flux, already discussed. And it is also deduced that the increase in the initial concentrations led to a very similar resistance values, not being significance this variable in the NF process, at least, in the range of concentrations tested. The values of R_f were slightly higher for the reservoir water, specially in the experiment performed with the hydrophobic CK membrane, which can be explained by the higher contribution of NOM adsorption to the overall fouling. Finally, the additional presence of humic acids and calcium ions also increased R_t and R_f due to the fact that the higher membrane fouling caused adsorption and formation of calcium complexes of humic acids as explained above.

The dominant fouling mechanism can be estimated from the results for the internal and external fouling resistances. Thus, it is observed that R_{ef} is considerably higher than R_{if}, specially for the hydrophilic DK and DL membranes. It indicates that the flux decline is mainly due to concentration polarization and cake layer formation on the membrane surfaces (herbicides and NOM present) that cause external membrane fouling. However, the contribution of R_{if} to the overall membrane fouling was significant, or even higher than R_{ef}, in the case of the hydrophobic CK membrane because of its higher adsorption capacity. As it was pointed out by Lee and Lee [23], the internal fouling plays a more important role in hydrophobic membranes, with high capacity of adsorption towards hydrophobic compounds like HA and phenyl-urea herbicides. Conversely, in the case of hydrophilic membranes, such as DL and DK, the adsorption capacity of materials is lower, and other mechanisms prevail in the retention of the micro-pollutants. On the other hand, the additional presence of humic acids and calcium ions also increased R_{if} due to their adsorption on the membranes.

3.2. Retention of herbicides and mass adsorbed on the membranes

The retention coefficients constitute a measure of the retention efficiency of a membrane in a filtration process. There are several factors affecting retention and the retentions mechanisms [24,25]. The main key solute parameters that primarily affect solute retention are molecular weight (MW), molecular size (length and width), acid disassociation constant (pK$_a$), hydrophobicity/hydrophilicity

($\log K_{ow}$) and polarity (dipole moment). Similarly, key membrane properties affecting retention are MWCO, pore size, surface charge (measured as zeta potential) and hydrophobicity/hydrophilicity (measured as contact angle). Therefore, the retention coefficients are an important tool to elucidate the retention mechanisms, and they can be calculated by comparing the permeate concentration of a specific substance with its concentration in the feed stream, according to the following expression:

$$R = \frac{C_f - C_p}{C_f} \times 100 \qquad (7)$$

where C_f and C_p are the concentrations of each herbicide in the feed and permeate solutions respectively. According to Eq. (7) the retention coefficients were evaluated for the phenyl-ureas at the steady state (that is, values calculated at VRF = 1.1), being the values obtained compiled in Table 4.

Firstly, the influence of the main operating variables on the retention coefficients can be established. Thus, the effect of the TMP can be deduced from experiments performed with the DK membrane (Expts. MDK-10-20-5, MDK-20-20-5 and MDK-30-20-5; or RDK-10-20-5, RDK-20-20-5 and RDK-30-20-5). Thus, the R factors increased with increasing TMP from 10 to 30 bar, which can be explained by considering that an increase in the TMP leads to an increase and compression of the fouling layer onto the membrane, which partially obstructs the permeation of solutes and leads to higher R values. With respect to the effect of temperature, it is observed in Fig. 3, which represents the experiments where the temperature was modified in the mineral water, that the increase in the temperature promotes a decrease in the R coefficients, as it has been reported previously [19]. This effect might be due to a decrease in the water viscosity at higher temperature which increases the permeate flux through the membrane as was already discussed, but decreases its retention capacity. Since the solubility of slightly soluble non-ionic chemicals increases with increasing temperature, the adsorption of these compounds on the membrane would decrease. Therefore, the change in the solubility could also decrease the retention of the investigated phenyl-urea herbicides. Regarding to the influence of the herbicides initial concentration on the retention, it is shown in Expts. MDK-20-20-5 and MDK-20-20-10, as well as in Expts. RDK-20-20-5 and RDK-20-20-10, that
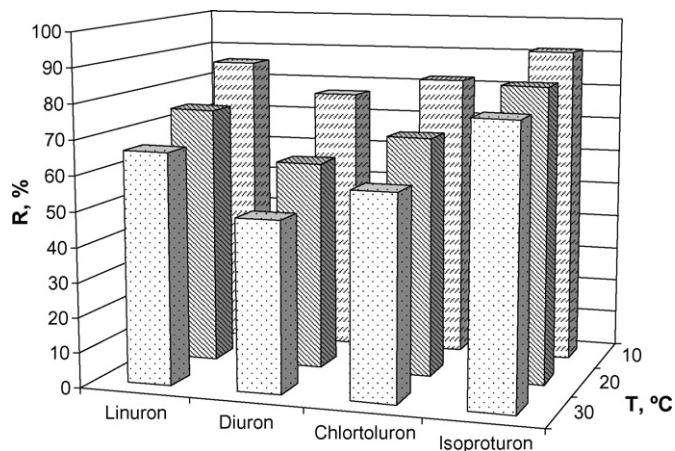
Fig. 3. Influence of temperature on the herbicides retention coefficients. Experiments MDK-20-10-5, MDK-20-20-5 and MDK-20-30-5.

there is a slight effect, with a smooth increase in the retention coefficient with the increase in this initial concentration only in the case of mineral water. And by considering the water matrix type, the results show higher retention coefficients in the reservoir water than in the mineral water as could be expected, because the reservoir water induces a higher fouling on the membranes due to NOM adsorption and pore blocking. This membrane fouling effect decreases the pore size and increases the herbicide retention. Moreover, these hydrophobic herbicides might form pseudocomplexes with the humic substances present in the reservoir water, thus increasing their retention [26]. In addition, the buildup of an organic layer (cake) on the membrane leads to the possibility that the adsorption of herbicides on this layer increases their retention.

The nature of the membranes promoted important differences in the values retention coefficients obtained, as it is shown in Fig. 4 for the reservoir water taken as example (Expts. RDK-20-20-5, RCK-20-20-5 and RDL-20-20-5). Thus, the DK and DL membranes (thin film composite membranes, hydrophilic character) exhibited in general, retentions higher than 50%, while the CK membrane (cellulose acetate membrane, hydrophobic character) provided retentions lower than 40%, except for linuron that were 71.2% and 79.9% for the mineral and reservoir water respectively. At the same time, the higher retention for the DK membrane compared to the DL membrane can be explained by its lower MWCO according to the data obtained by Petrinic et al. [10], these values being 230
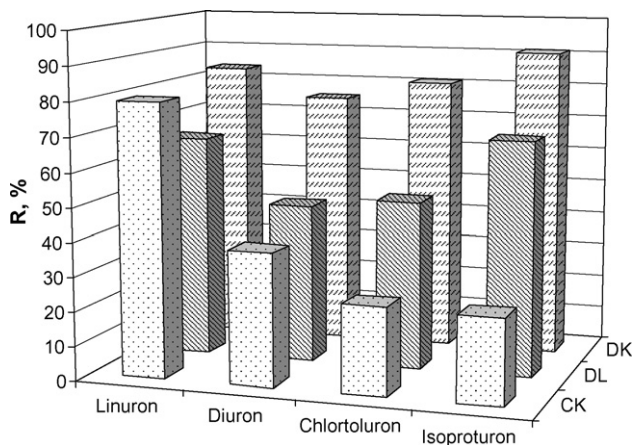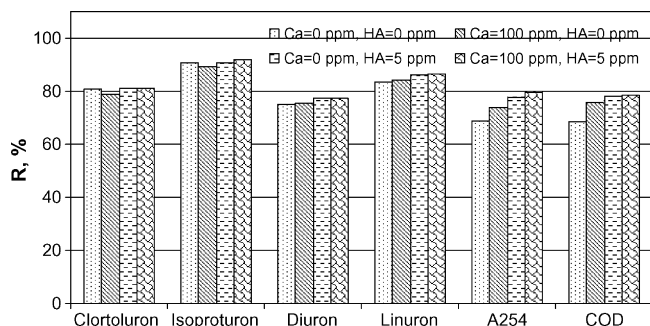
and 340 Da for DK and DL membranes, respectively. In effect, a membrane with small pores rejects a larger amount of organic pollutants; on the contrary, if the pores are larger, the molecules pass more easily through the membrane.

Also, the nature of the membranes is the main cause of the different herbicides retention trends. Thus, the retention order for the DK and DL membranes (hydrophilic character) was isoproturon > linuron > chlortoluron > diuron, as it can be also observed in Fig. 4. It has been reported [24,25] that an important parameter that influences the retention in nanofiltration is the molecule polarity, whose increase provided a decrease in the retention. According to these results, the most polar molecules (those with higher dipole moments) yielded lower retentions. A plausible explanation for this effect is proposed, by considering electrostatic attractions [25]: the dipole is directed to the membrane charge in such a way that the side of the dipole with the opposite charge is closer to the membrane. The dipole is thus directed towards the pore and enters more easily into the membrane structure. Because entry into the membrane structure is thus facilitated, a higher fraction of polar molecules permeates through the membrane in comparison to non-polar substances, and consequently, leading to a lower retention of these polar solutes.

In order to confirm whether this mechanism was the main responsible for the retention trends obtained for the DK and DL membranes of the present study, the polarity of the selected herbicides was evaluated by determining the dipole moment, by using the computer program Hyperchem, as it has been previously mentioned. The values obtained (see Table 1) were 3.31, 4.76, 4.92 and 5.87 Debye for isoproturon, linuron, chlortoluron and diuron respectively (see Table 1). According to these values, diuron is the most polar compound, and at the same time, presented the lowest retention. On the contrary, isoproturon, which is the least polar compound, reached the highest retention. As a consequence, the molecule polarity is a key parameter for the retention of herbicides by the hydrophilic DK and DL membranes.

However, for the CK membrane (hydrophobic character), the retention efficiency follows this sequence: linuron > diuron > chlortoluron > isoproturon, which coincides with the sequence of molecular weights (see Table 1). In the case of hydrophobic membranes it can be expected that instead of polarity, the dominant mechanism for retention 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, being the molecular weight the most accessible parameter that indicates the size of a molecule [24,25]. Similar results, based on sterical hindrance and size exclusion effects, were reported by Zhang et al. [20] for the retention of simazine and atrazine in filtration experiments of these herbicides. In addition, the hydrophobic nature of this membrane must favor the adsorption of hydrophobic compounds, as the herbicides of the present study: in effect, as it is observed the retention sequence also coincides with the increasing hydrophobic character of the herbicides (see log K_{ow} in Table 1). In conclusion, the retention of hydrophobic solutes, as the herbicides of the present study, by hydrophobic membranes could be predicted using the molecular weight of the compounds and log K_{ow}, as well as the hydrophobic character of the membranes which may also influence the retention because of their capacity to adsorb hydrophobic compounds [6,27].

The influence of the presence of high concentrations of humic acids and calcium ions in the experiments performed with the DK membrane and the reservoir water can be deduced from the R coefficients depicted in Fig. 5. While the retention of chlortoluron and isoproturon was similar in this group of experiments, the retention of linuron and diuron seems to increase slightly in the presence of calcium ions and humic acids, although the

Fig. 4. Influence of the nature of membranes on the herbicides retention coefficients. Experiments RDK-20-20-5, RCK-20-20-5 and RDL-20-20-5.

Fig. 5. Effect of the additional presence of calcium and humic acids on the retention of herbicides and water quality parameters in the reservoir water. Experiments RDK-20-20-5-Ca, RDK-20-20-5-HA and RDK-20-20-5-Ca-HA.

difference is not statistically significant. This is attributed to the formation of complexes between humic acid and herbicides (specially with those more hydrophobic such as linuron and diuron), which enhances the retention by size exclusion [1,26]. Therefore, the retention of hydrophobic herbicides should be grater when treated together with humic acids. Similarly, the improvement in the herbicide retention when treated together with calcium ions can be attributed to the retention of the divalent ions, which block the membrane pores. Moreover, at high cation concentrations there is a decrease in the electrostatic forces observed inside the membranes, which leads to the reduction of the active pores and consequently to the reduction of the membrane permeability [28].

The compounds adsorption can be evaluated in order to establish the contribution of this mechanism to the global retention of the solutes by the membranes used. For this purpose, mass balances based on the concentration of each herbicide in feed, retentate and permeates streams are applied; and the adsorbed mass is defined as the amount of solute adsorbed per unit area onto the membrane surface and into the membrane pores, according to the expression [1,2]:

$$M_{ads} = \frac{(C_f V_f) - \left[\left(C_p V_p \right) + (C_r V_r) \right]}{A} \tag{8}$$

where V_f, V_p, and V_r are the feed, permeate and retentate volumes; C_f, C_p, and C_r are the feed, permeate and retentate concentrations for each herbicide, M_{ads} is the amount of solute adsorbed per unit membrane area, and A is the effective membrane area. At the same time, the adsorption percentage (AP) was also determined by the

expression [1]:

$$AP = \frac{(C_f V_f) - \left[\left(C_p V_p \right) + (C_r V_r) \right]}{C_f V_f} \times 100 \tag{9}$$

Table 5 summarizes the results obtained for M_{ads} and AP in the experiments performed. The values reported cover a wide range of M_{ads} and AP, depending on the experimental conditions applied, but some trends are clearly observed. Thus, higher M_{ads} and AP values were obtained for the CK membrane, as could be expected, due to its hydrophobic nature: the adsorption is mainly enhanced by hydrophobic interactions between hydrophobic compounds and the hydrophobic region of the membranes. And much lower values were found for DK and DL membranes, due to their hydrophilic nature.

Additionally, the M_{ads} sequence for the herbicides tested in all the experiments in the three membranes for both water matrices, mineral and reservoir, was: linuron > diuron > chlortoluron > isoproturon, which agrees with the hydrophobic character of these compounds measured by $\log K_{ow}$ (Table 1). In the case of the hydrophobic CK membrane, this sequence agrees with that obtained for the retention coefficients, confirming that the adsorption is the predominant mechanism for the retention of herbicides by this membrane. On the contrary, in the DK and DL membranes, the retention coefficient sequence is different to that of adsorption; and therefore, it is an indication that other mechanisms than adsorption, such as size exclusion and polarity, are the responsible for the retention of the herbicides, as was previously discussed.

3.3. Retention of other water quality parameters

In order to evaluate the final quality of the permeate, the reduction of some NOM parameters such as DOC and $UV_{254\,nm}$ absorbance were measured in the experiments performed with the reservoir water (higher NOM content). The retention coefficients of these quality parameters are summarized in Table 6. DOC retentions are in the range 20–80% and $UV_{254\,nm}$ retentions in the range 50–80%. The effects of the operating conditions on the retention of DOC and $UV_{254\,nm}$ absorbance were similar to the already discussed for the retention of herbicides: positive of TMP, negative of temperature and lower retention for the CK membrane. DOC retention was lower than $UV_{254\,nm}$ retention in the experiment performed with the hydrophobic CK membrane since the UV absorbance at 254 nm is mainly due to the adsorption by aromatic/hydrophobic compounds, whereas DOC measures the concentration of overall

Table 5
Amount of solutes adsorbed per unit area (M_{ads}) and adsorption percentages (AP) in the NF of phenyl-ureas.

Experiment	Linuron		Diuron		Chlortoluron		Isoproturon	
	M_{ads} (µmol m^{-2})	AP (%)	M_{ads} (µmol m^{-2})	AP (%)	M_{ads} (µmol m^{-2})	AP (%)	M_{ads} (µmol m^{-2})	AP (%)
MDK-10-20-5	80.7	15	65.2	12	55.6	10	50.9	9
MDK-20-20-5	82.0	15	73.7	13	61.2	11	61.3	11
MDK-30-20-5	82.5	15	79.7	14	73.9	13	72.1	13
MDK-20-10-5	102.3	19	98.1	18	91.6	17	89.2	16
MDK-20-30-5	91.6	17	64.1	12	64.0	12	58.6	11
MDK-20-20-10	279.3	26	219.0	20	198.1	18	169.2	16
MCK-20-20-5	235.5	44	101.1	19	75.4	14	73.8	14
MDL-20-20-5	115.6	22	75.1	14	63.0	12	62.5	12
RDK-10-20-5	140.4	26	83.6	16	69.8	13	69.7	13
RDK-20-20-5	139.4	26	94.3	18	85.9	16	82.5	15
RDK-30-20-5	136.4	25	98.0	18	86.1	16	84.6	16
RDK-20-10-5	137.9	25	111.1	21	93.2	18	90.8	17
RDK-20-30-5	143.3	26	91.4	17	85.3	16	82.1	15
RDK-20-20-10	226.9	20	115.2	11	101.1	9	95.1	9
RCK-20-20-5	254.3	47	113.8	21	106.3	20	101.0	19
RDL-20-20-5	144.9	27	85.3	16	78.6	15	72.6	14

Table 6
COD and $UV_{254\,nm}$ removal efficiency (%) in the experiments performed with the selected membranes and the reservoir water.

Experiment	Membrane	DOC (%)	$UV_{254\,nm}$ (%)
RDK-10-20-5	DK	66.9	66.3
RDK-20-20-5	DK	70.5	68.8
RDK-30-20-5	DK	79.5	75.4
RDK-20-10-5	DK	76.0	76.4
RDK-20-30-5	DK	70.6	67.8
RDK-20-20-10	DK	70.6	69.1
RCK-20-20-5	CK	18.6	51.5
RDL-20-20-5	DL	69.1	61.8
RDK-20-20-5-Ca[a]	DK	75.9	73.9
RDK-20-20-5-HA[b]	DK	78.2	77.5
RDK-20-20-5-Ca-HA[c]	DK	78.5	79.7

[a] Addition of $100\,mg\,L^{-1}$ Ca^{2+}.
[b] Addition of $5\,mg\,L^{-1}$ HA.
[c] Addition of $100\,mg\,L^{-1}$ Ca^{2+} and $5\,mg\,L^{-1}$ HA.

compounds. In addition, the low retention of DOC for CK confirms the fact that this membrane has larger pores. However, DOC retention was slightly higher than $UV_{254\,nm}$ retention in the experiments performed with the hydrophilic DK and DL membranes because of its reduced capacity to adsorb aromatic/hydrophobic compounds. Therefore, size exclusion must be the main retention mechanism for high MW compounds. The additional presence of humic acids and calcium ions increased the retention of both DOC and $UV_{254\,nm}$ absorbance (Fig. 5) due to the formation of complexes and adsorption on the membranes as commented above. It must be noticed that the significant removal of NOM, especially hydrophobic and aromatic compounds, reduces the disinfection by-products formation potential in the final water.

In conclusion, under a point of view of the retention coefficients, the DK membrane was obviously the most appropriate membrane for the removal of phenyl-urea herbicides from natural waters, especially the most polar compounds (retention of isoproturon above 90%). Additionally, this membrane also provided high retentions for DOC (around 70%) and aromatic organics (UV absorbance at 254 nm). However, a concentrated fraction with high content in hazardous materials is also produced, which needs special treatment such as chemical oxidation with ozone [29] before its disposal.

4. Conclusions

Nanofiltration cross-flow experiments were performed for the elimination of four phenyl-urea herbicides (linuron, diuron, chlortoluron and isoproturon) when present in a commercial mineral water and in a reservoir water. It was determined that VRF = 1.1 provided the steady-state permeate flux, which values ranged from 23.8 to $81.4\,L\,h^{-1}\,m^{-2}$ depending on the operating conditions. The lowest values for the total resistances to the permeate flux corresponded to the DL membrane, while the CK and DK membranes presented higher total resistances. More specifically, the partial contribution of the fouling resistance was smaller than the contribution of the inherent resistance of the clean membrane, which confirms that the membrane fouling is low in experiments with model compounds dissolved in different water types.

It was found that the retention order for the DK and DL membranes (hydrophilic character) was isoproturon > linuron > chlortoluron > diuron, being the molecule polarity the main parameter that influences on the retention. On the contrary, the retention efficiency in the CK membrane (hydrophobic character) followed the sequence: linuron > diuron > chlortoluron > isoproturon, which indicates that, instead of polarity, the main responsible for retention is the MW and the adsorption ($\log K_{ow}$). Moreover, the mass

adsorbed sequence found in the three membranes for both water matrices was: linuron > diuron > chlortoluron > isoproturon. From the results obtained, it can be concluded that the DK membrane was the most adequate for the phenylureas elimination from natural waters, especially for the most polar compounds, yielding higher retention coefficients as well as higher retentions for DOC and aromatic compounds.

Finally, the additional presence of humic acids and calcium ions increases membrane fouling, which is a consequence of the adsorption of species (NOM and ions onto the membrane) as well as pore blocking and formation of a cake layer on the membrane surface. However, the effect of humic acids and calcium ion on the retention coefficients is not significant, especially for the less hydrophobic compounds (chlortoluron and isoproturon).

Acknowledgements

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