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Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration

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ABSTRACT

This study evaluates the efficiency of nanofiltration to remove pesticides and polycyclic aromatic hydrocarbons (PAHs) from drinking water sources with different compositions (groundwater, spring water, surface water, and surface water after sedimentation) as well as the main mechanisms governing the rejection of these compounds. All the polycyclic aromatic hydrocarbons compounds were highly removed from the different water matrices due to strong hydrophobic interactions between these compounds and the membrane. Lower and variable rejections were obtained for pesticides in different natural water matrices. Atrazine rejection was found to be independent from the water matrix composition and appears to be influenced by a combined effect of hydrophobic and coulombic interactions with the membrane as well as size exclusion. The rejection of alachlor may be related to the composition of the water in terms of ionic content. The ions present in the water may have a "shielding" effect on the solute and membrane surface charge, reducing the repulsive electrostatic interactions and therefore, decreasing the rejection of alachlor in the matrices with higher alkalinity. The main mechanism of pentachlorophenol rejection is the hydrophobic interaction with the membrane, although electrostatic interactions cannot be excluded because pentachlorophenol is deprotonated at the pH of the water matrices. This work clearly shows that the composition of the water matrices may highly influence the efficiency of the nanofiltration process in terms of the removal of the micropollutants.

Keywords: Pesticides; Polycyclic aromatic hydrocarbons; Nanofiltration; Natural water sources; Water treatment

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1. Introduction

Several pesticides and polycyclic aromatic hydrocarbons (PAHs) have been considered emerging contaminants by the US Environmental Protection Agency and the European Union. Pesticides such as atrazine, alachlor, and pentachlorophenol as well as the polycyclic aromatic hydrocarbons naphthalene, anthracene, fluoranthene, benzo(*a*)pyrene, and benzo(*g*,*h*,*i*)perylene are considered priority pollutants by the European Water Framework Directive 2000/60/EC because they are highly toxic, persistent in the environment, and have the

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potential to bioaccumulate within an organism, threatening the aquatic environment and human health [1]. PAHs became especially concerning due to their toxic, carcinogenic, and mutagenic properties. Higher molecular weight PAHs are considered genotoxic compounds, being benzo(*a*)pyrene often referred to as one of the most potent carcinogenic known [2].

These xenobiotics have been detected in drinking water sources such as groundwater and surface water. The concentrations of PAHs in these source waters have been reported in the range of 10–250 ng/l [3] whereas atrazine, alachlor, and pentachlorophenol have been detected at occurrence levels varying from 2 to 13,000 ng/l [4,5].

In the last years, pressure driven membrane processes such as nanofiltration (NF) and reverse osmosis have become promising technologies to remove organic and inorganic micropollutants from drinking water [6]. A considerable number of studies have reported the removal of trace organic contaminants by these pressure driven membrane processes [7–12].

Nanofiltration has been reported as an efficient process to efficiently remove pesticides from water. Several publications have reported atrazine removal by different NF membranes from synthetic waters [8,13–16], surface water [17], and groundwater [11,18]. Variable rejections from 10.9% to 97.5% were obtained for this molecule. To the best of our knowledge, there are no studies concerning the removal of the priority pesticides alachlor and pentachlorophenol by NF membranes and only two publications have reported the efficiency of the NF membrane Desal 5DK to remove atrazine [19,20]. Boussahel et al. [19] reported an atrazine removal higher than 90% in laboratory grade water and synthetic water while Berg et al. [20] obtained a rejection of approximately 40% using waters with very different dissolved organic carbon concentrations.

Very few studies have been conducted to evaluate NF efficiency on the removal of the PAHs mentioned above [17,21]. Yoon et al. [17] reported a high degree of rejection for some PAHs in experiments using three different sources of surface water and an ESNA membrane. Very high removals of benzo(*a*)pyrene, anthracene, and naphthalene were achieved with all surface water sources. Concerning benzo(*g*,*h*,*i*)perylene, there are no reports discussing the use of nanofiltration for its removal.

Nanofiltration experiments are often conducted using individual compounds. Even though some studies have reported low differences between the rejection of individual compounds and compounds in mixtures [8,15–17], the use of mixtures simulates better the conditions in a drinking water treatment facility since a wide combination of compounds is expected to be found in the environment, where interaction and competition effects may occur.

Parameters such as molecular size, polarity, and hydrophobicity of the solute as well as the molecular weight cut-off and charge of the membrane have been mentioned as the main factors affecting the rejection of uncharged organic compounds.

The properties of the water matrix are also expected to have an important role in the rejection, particularly the levels of natural organic matter (NOM), ionic composition, and pH [14,22]. Most studies addressing the nanofiltration potential for the removal of organic compounds from water have been conducted in laboratory grade water and synthetic water matrices spiked with NOM and various ions at different pH values, which facilitates the understanding of the effect of each parameter in the rejection, since the exact composition of the water matrix is known. However, the commercial humic and fulvic acids usually used in these studies to address the effect of NOM may not be representative of the natural organic matter found in real water matrices [13]. In addition, the combined effect of the different ions present in real water matrices may also influence the rejection. Although several studies addressing the effectiveness of nanofiltration membranes to remove trace organic contaminants have been reported, few studies using different natural water sources such as surface water, groundwater, and spring water have been reported to date [7,11,17–19]. Since the removal of the priority micropollutants from water is extremely important, further studies should be conducted to provide a better understanding of the main parameters and mechanisms that influence the rejection of these compounds in real water matrices mimicking the conditions in water treatment plants.

This study reports the effectiveness of the nanofiltration membrane Desal 5DK to remove priority PAHs (naphthalene, anthracene, fluoranthene, benzo(*a*)pyrene, and benzo(*g*,*h*,*i*)perylene) and pesticides (atrazine, alachlor, and pentachlorophenol) selected due to their very different structures and physico-chemical properties, spiked as individual compounds and mixtures into laboratory grade water and natural water sources with very different compositions such as groundwater, spring water, surface water, and surface water collected after the sedimentation process. The rejections obtained are discussed in terms of the structure and physico-chemical properties of the organic compounds, interactions between the molecules and the membrane, and real water matrix characteristics. Concerning the solute properties, molecular weight (MW), dipole moment (μ), octanol-water partition coefficient (Log K_{ow}), and acid constant (pK_a) are the main properties addressed while for the water matrices, the concentration of organic matter, alkalinity, and hardness were considered. The influence of hydrophobic and of electrostatic interactions between the organic compounds and the membrane are discussed.

2. Experimental section

2.1. Reagents

The selected pesticides and PAHs were purchased as solutions or solids of the highest grade commercially available (higher than 98.9%, Sigma Aldrich, Germany).

Laboratory grade water was produced by a bidistilled water system (Millipore, CA, USA). The natural water matrices–spring water, groundwater, surface water, and surface water collected after sedimentation—with very different compositions were supplied by the drinking water utility Empresa Portuguesa das Águas Livres that treats and supplies drinking water to approximately 2.5 million people. The real water samples were collected in brown glass bottles and stored at 4°C until used.

2.2. Analytical methods

The analytical methods used to detect and quantify the selected PAHs and pesticides in the feed, permeate, and retentate samples were previously described [23].

Briefly, the PAHs were analyzed by reverse-phase high performance liquid chromatography using fluorescence detection after sample concentration by liquid–liquid extraction using dichloromethane or solid phase extraction using OASIS HLB cartridges (Waters, MA, USA; 6 ml; 200 mg) and an eluting mixture of dichloromethane/propanol. A chromatographic LichroCart® 250-4 LiChrospher® PAH column (Merck, Germany) with 250 mm of length was used with the following mobile phase composition: 0–3 min, acetonitrile/water 1:1; 15–30 min, 100% acetonitrile. The flow rate was 1 ml/min and the oven temperature was set at 20°C during the first 10 min and 28°C from 10 to 30 min.

The detection of the analytes, atrazine and alachlor was accomplished by gas chromatography with mass spectrometry in selected ion monitoring mode (SIM) using a HP-5MS column with 60 m × 0.25 mm × 0.25 μm (Agilent Technologies, CA, US). The chromatographic detection of these compounds was preceded by solid phase extraction using an Autotrace workstation system (Caliper Life Sciences, UK), OASIS HLB cartridges and a mixture of *n*-hexane and dichloromethane as eluting solvents. The temperature programme starts with 30°C, which is held during 1 min. A heating rate of 50°C/min is performed from 30 to 170°C and then, 170°C is held during 1 min. The following heating rate of 1°C/min from 170 to 190°C is performed and the temperature of 190°C is held for 3 min. The last heating rate was 50°C/min from 190°C to 250°C, which is held during 10 min.

Ten microlitre of HCL (15%) and 2 g of sodium chloride were added to the samples containing pentachlorophenol prior to the concentration by solid phase microextraction using 85 μm polyacrilate fibre. Gas chromatography with electron capture detection was used for the analysis of pentachlorophenol, using a HP-5MS column with 30 m × 0.32 mm × 0.25 μm (Agilent Technologies, CA, US). The temperature programme starts with 40°C during 5 min, followed by a heating rate of 5°C/min until 210°C, which is held during 3 min.

2.3. Nanofiltration experiments

Filtration experiments were conducted in a stainless steel dead-end stirred-cell (Membrane Extraction Technology Ltd., UK) with an effective membrane area of 54 cm^2. This cell was connected to an HPLC pump (Kratos Analytical Spectroflow 400, Germany), which continuously pumped the feed solution into the cell during nanofiltration.

The nanofiltration flat-sheet membrane Desal 5DK (GE Osmonics, USA) was used to address the removal of the selected pesticides and PAHs. These are thin film composite membranes with a polysulphone support layer. Desal 5DK has a molecular weight cut-off of 150–300 Da [19] and it is negatively charged at neutral pH (information provided by the manufacturer). Therefore, Desal 5DK may be considered as a "loose" membrane which combined with its non-uniformity may affect the rejection of the organic compounds. In each experiment, a new membrane was used to avoid the presence of adsorbed compounds on the membrane from previous experiments. Prior to use, membranes were washed with laboratory grade water to remove any preservatives and were placed on top of a stainless steel porous disk. Before each experiment, laboratory grade water was processed at 10 bar until a constant flux was achieved. The mean clean water permeability determined for Desal 5DK was $3.44 \pm 0.05\ l\ h^{-1}\ bar^{-1}\ m^2$, at 21 ± 2°C.

The different water matrices were spiked with the appropriate volume of the compounds stock solutions to achieve the following concentrations: 20 μg/l for PAHs, 75 μg/l for atrazine and alachlor, and 150 μg/l for pentachlorophenol. These concentrations were set based on the detection limits of the analytical methods. The organic compounds were grouped and spiked in the water matrices according to their common analytical methods. Different feed solutions were therefore prepared with pentachlorophenol, a mixture of atrazine and alachlor, and a mixture of the PAHs and placed in brown glass bottles to avoid the degradation of the compounds by light. The rejection of atrazine as an individual compound was also accessed and compared with the rejection of this compound in the presence of alachlor. These solutions were fed to the cell and stirred at 400 rpm during approximately 30 min, without applying a pressure difference, to allow the contact between the membrane and the feed solution.

All experiments were conducted at 10 bar and room temperature (21 ± 2°C). The feed solutions were stirred at 400 rpm to minimize concentration polarization phenomena. A constant feed volume of 200 ml was maintained inside the cell during the experiments (5–15 h). All experiments were conducted as single experiments.

To evaluate the risk of degradation of organic compounds present in the feed water, during the nanofiltration process, 100 ml of the feed solution were used as control. In the beginning of the experiment, 50 ml of the control solution (initial control) were taken to an amber flask and were immediately acidified to pH 2–3 with sulphuric acid, which prevents the degradation of organic compounds that may occur due to the presence of microorganisms in the untreated source waters. This solution was then stored at 4°C until analysis. The remaining 50 ml (final control) were transferred to another amber flask and kept during the nanofiltration procedure at the same experimental conditions as the solution that was filtered in terms of temperature (room temperature) and light exposure (in the dark). The same level of degradation was therefore expected to occur in this control and in the solution fed to the nanofiltration system. This final control was only acidified with sulphuric acid at the end of the filtration procedure and stored at 4°C until analysis. The degradation of the organic compounds during several hours of filtration was accessed by determining and comparing the concentration of the organic compounds in the initial and final control solutions. Noticeable differences in the concentration of the controls were not detected, showing that degradation of the selected compounds did not occur during the nanofiltration experiments conducted.

After nanofiltration, samples of feed, permeate, and retentate were acidified at pH 2–3 with sulphuric acid and stored at 4°C prior to analysis, to avoid the degradation of the compounds.

The apparent rejection (R) of the selected compounds was determined using Eq. (1).

$$R(\%) = 100 \times \left(1 - \frac{C_\mathrm{p}}{C_\mathrm{f}}\right) \tag{1}$$

where C_p and C_f are the concentrations of a given compound in the permeate and feed, respectively.

The percentage of rejection due to adsorption to the membrane surface (A) was determined using Eq. (2):

$$A(\%) = 100 \times \left(1 - \frac{C_\mathrm{p}V_\mathrm{p} + C_\mathrm{r}V_\mathrm{r}}{C_\mathrm{f}V_\mathrm{f}}\right) \tag{2}$$

where C_p, C_r, and C_f are the concentration of a given compound in the permeate, retentate, and feed, respectively, whereas V_p, V_r, and V_f are the volume of permeate, retentate, and feed, respectively.

3. Results and discussion

The selected PAHs and pesticides have very different structures and physico-chemical properties. The properties of these compounds such as molecular weight, octanol–water partition coefficient, and dipole moment are detailed in Table 1.

Three natural water sources with very different compositions in terms of their total organic carbon, turbidity, alkalinity, and total hardness were selected (Table 2).

The surface water presented the higher levels of total organic carbon and turbidity, while the spring water and groundwater samples showed high alkalinity and total hardness.

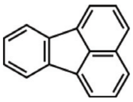
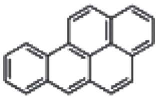
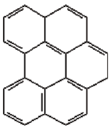
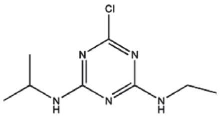
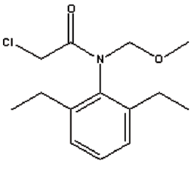
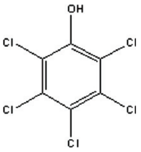
Nanofiltration of the groundwater and spring water matrices could be accomplished directly (without the need for pre-treatments). The higher levels of turbidity and natural organic matter of the surface water matrix led to an extremely high decrease in permeate flux and membrane fouling. The nanofiltration of surface water without pre-treatment was therefore only tested for one of the selected pesticides: pentachlorophenol. Conventional surface water treatment often includes coagulation, flocculation, and sedimentation processes. The best place to install a membrane filtration system, in a water treatment utility that treats water with high levels of turbidity and NOM besides being subject to seasonal variability, would be after sedimentation to minimize fouling problems. Rejection of all the selected PAHs and pesticides was also therefore tested in surface water collected after the coagulation, flocculation, and sedimentation processes. After the sedimentation process the levels of organic matter and suspended solids are expected to be very low compared to the untreated water (closer to the groundwater matrix composition) but the ionic composition is likely to be very similar to the untreated surface water (see Table 2).

Table 3 and Fig. 1 show the Desal 5DK nanofiltration rejection percentages of the chosen PAHs and pesticides spiked in different water matrices, calculated using Eq. (1).

Extremelly high rejections were determined for PAHs (Table 3) while variable rejections were obtained for the pesticides in the different water matrices (Fig. 1).

The concentration of PAHs in the permeate was often found to be lower than the detection limits of the analytical methods, showing that total removal or at least removals higher than 98% were obtained in the real water matrices tested. PAHs are very nonpolar and hydrophobic compounds (octanol–water partition coefficients are shown in Table 1), being likely to adsorb on the membrane surface. They adsorb to virtually any surface since their adsorbed state is energetically preferable to the state in which water interactions take place. As shown in Table 4, the rejection of these compounds due to adsorption, calculated using Eq. (2), is always higher than 72%.

Table 1
Physico-chemical properties of the selected priority PAHs and pesticides

Compound	Molecular formula	Molecular weight (Da)	Log K_{ow}	Dipole moment (D)	pK_a
 Naphthalene	$C_{10}H_8$	128.2	3.36[24]	–	–
 Anthracene	$C_{14}H_{10}$	178.2	4.54[24]	–	–
 Fluoranthene	$C_{16}H_{10}$	202.3	5.22[24]	–	–
 Benzo(a)pyrene	$C_{20}H_{12}$	252.3	6.50[24]	–	–
 Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.3	6.63[24]	–	–
 Atrazine	$C_8H_{14}ClN_5$	215.7	2.56[24]	2.8[25]	1.70[15]
 Alachlor	$C_{14}H_{20}ClNO_2$	269.8	3.52[26]	4.2[27]	0.62[28]
 Pentachlorophenol	C_6HCl_5O	266.3	5.12[29]	1.9[30]	4.70[31]

Therefore, the main mechanism for the rejection of the PAHs is the hydrophobic interaction of these compounds with the membrane, causing their adsorption, which is in accordance with previous studies that addressed the removal of some of these PAHs from different sources of surface water and a synthetic water [17,21].

The rejections obtained for the PAHs in laboratory grade water were slightly lower when compared to real water matrices, which may be explained by the adsorption of PAHs on NOM colloids, present in the natural water matrices. In laboratory grade water, fluoranthene was the less rejected compound, which is also in accordance with a previous study by Yoon et al. [17].

Although very high rejections were obtained for the PAHs in this work, further research should address if such high rejections are maintained for long-term operation processes. Chang et al. [32] and Kimura et al. [33] concur with the need to conduct further studies to address membrane efficiency under saturation conditions.

Table 2
Chemical characterization of the natural water sources tested: groundwater, spring water, and surface water

Physico-chemical properties	Groundwater	Spring water	Surface water
Total organic carbon (mg/l C)	<1.00 ± 0.18	1.00 ± 0.18	3.56 ± 0.36
Dissolved solids (mg/l)	376	404	512
Turbidity (NTU)	<0.400 ± 0.032	<0.40 ±0.032	12.5 ± 1.0
Alkalinity (mg/l CaCO$_3$)	231 ± 18	209 ± 17	87.8 ± 7.0
Conductivity (µS/cm 20°C)	525 ± 26	564 ± 28	715 ± 36
Total Hardness (mg/l CaCO$_3$)	267	236	209
pH	7.44 ± 0.25	7.34 ± 0.24	7.90 ± 0.26
Suspended solids (mg/l)	<2.0	<2.0	13
Calcium (mg/l)	90.0 ± 11	80.0 ±9.6	51.3 ± 6.2
Magnesium (mg/l)	10.4 ± 1.6	8.8 ± 1.3	19.7 ± 3.0
Temperature (°C)	20.3	17.7	22.4
Colour (mg/l Pt–Co)	<2.00 ± 0.19	<2.00±0.19	6.52 ± 0.62
Temperature of pH determination (°C)	18.4	18.2	19.8
Oxidability (mg/l O$_2$)	0.520 ± 0.078	0.630 ± 0.095	3.69 ± 0.55
Biochemical oxygen demand (mg/l O$_2$)	<2.00 ± 0.46	<3.0 ± 0.7	<3.0 ± 0.7
Amoniacal nitrogen (mg/l NH$_4$)	<0.070 ± 0.014	<0.070 ± 0.014	<0.070 ± 0.014
Nitrites (mg/l)	<0.00500 ± 0.00060	0.0357 ± 0.0036	0.0228 ± 0.0023
Nitrates (mg/l)	3.09 ± 0.37	8.83 ± 0.62	2.93 ± 0.35
Chemical oxygen demand (mg O$_2$/l)	16	<5.0	11
Chloride (mg/l)	34.0 ± 3.4	60.2 ± 4.8	91.3 ± 7.3
Phosphorous (µg/l)	<50 ± 10	<375 ± 68	505 ± 91
Total Phosphorous (mg/l)	–	–	0.263
Sulphate (mg/l)	23.6 ± 1.9	13.4 ± 2.0	153.0 ± 9.2
Silica (mg/l)	7.9 ± 1.4	6.1 ± 1.1	<4.28 ± 0.77
Fluor (µg/l)	110 ± 19	104 ± 14	182 ± 18
Hydrogen sulphur (µg/l)	<4.0	<4.0	<4.0
Kjeldahl nitrogen (mg/l)	0.6	0.41	1.2
Sodium (mg/l)	20.6 ± 2.1	39.7 ± 4.0	68.3 ± 6.8
Potassium (mg/l)	<1.11 ± 0.11	1.76 ± 0.18	5.47 ± 0.55
Aluminium (µg/l)	<55.5 ± 7.8	<55.5 ± 7.8	855 ± 120
Iron (µg/l)	<55.5 ± 7.8	<55.5 ± 7.8	746 ± 104
Dissolved iron (µg/l)	<20.0	<20.0	<20.0
Manganese (µg/l)	<5.55 ± 0.56	<5.55 ± 0.56	33.3 ± 3.3
Zinc (µg/l)	<55.5 ± 5.6	<55.5 ± 5.6	<55.5 ± 5.6
Barium (µg/l)	26.6 ± 2.1	12.9 ± 1.0	21.7 ± 1.7
Cadmium (µg/l)	<0.100 ± 0.020	<0.100 ± 0.020	<0.100 ± 0.020
Lead (µg/l)	<2.00 ± 0.40	<2.00 ± 0.40	<2.00 ± 0.40
Cooper (µg/l)	<11.1 ± 1.3	<11.1 ± 1.3	<11.1 ± 1.3
Chromium (µg/l)	<2.00 ± 0.40	<2.00 ± 0.40	<2.00 ± 0.40
Nickel (µg/l)	<3.00 ± 0.45	<3.00 ± 0.45	<3.00 ± 0.45
Mercury (µg/l)	<0.200 ± 0.040	<0.200 ± 0.04	<0.200 ± 0.04

The behaviour of the three selected pesticides–atrazine, alachlor, and pentachlorophenol—varied in terms of the percent rejections, obtained in different water matrices (Fig. 1).

Even though atrazine rejection was found to be matrix independent, the rejections of alachlor and pentachlorophenol changed according to the matrix in which they were spiked showing that matrix composition can significantly influence the nanofiltration efficiency. In laboratory grade water, the total percent rejection obtained for the different pesticides increased with their molecular weight showing the influence of size exclusion mechanisms in the micropollutants retention.

The rejection obtained for atrazine was very similar in all the water matrices tested, which suggests that its rejection is fairly independent from the water composition. Berg et al. [20] reported a constant percent rejection of approximately 40% (extremely similar to the values observed in our experiments) for atrazine spiked in water with different dissolved organic matter

Table 3
Rejection of the selected PAHs in the different water matrices: laboratory grade water, groundwater, spring water, and surface water collected after sedimentation

Compound	Laboratory grade water	Groundwater	Spring water	Surface water after sedimentation
Naphthalene	>99.78	>99.87	>99.88	>99.67
Anthracene	95.73	>99.99	99.56	>99.90
Fluoranthene	77.83	>99.96	>99.92	>99.96
Benzo(*a*)pyrene	97.11	>99.99	>99.95	>99.98
Benzo(*g*,*h*,*i*)perylene	90.90	>99.93	>98.00	>99.92

Table 4
Rejection of the selected pesticides and PAHs due to adsorption on the membrane

Compound	% Adsorption
Atrazine	25.1[a]; 30.3[b]
Alachlor	0[b]; 31.0[a]
Pentachlorophenol	42.7[c]
Naphthalene	99.4[c]
Anthracene	94.2[c]
Fluoranthene	72.9[c]
Benzo(*a*)pyrene	92.1[c]
Benzo(*g*,*h*,*i*)perylene	77.7[c]

[a] Surface water after sedimentation.
[b] Groundwater.
[c] Laboratory grade water.

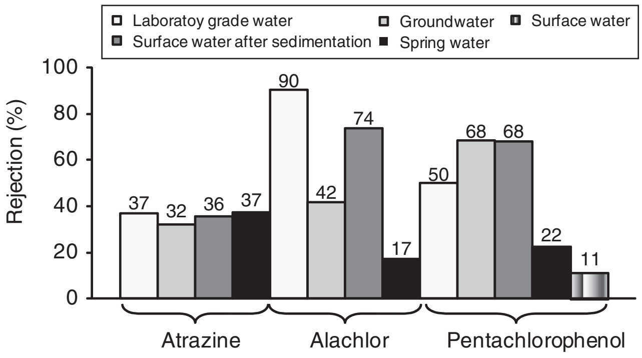


Fig. 1. Rejection of the pesticides atrazine, alachlor, and pentachlorophenol in laboratory grade water and different natural water sources: surface water after sedimentation, groundwater, spring water, and surface water.

concentrations using Desal 5DK. In other studies conducted using the same membrane and other nanofiltration membranes, no significant differences were also reported in the rejection of atrazine spiked in distilled water, synthetic waters, and real water matrices [7,14,19].

The removal of atrazine from the surface water after sedimentation was determined in a single solute feed and as a mixture of atrazine and alachlor to understand if, when present as a mixture, competition for the membrane could occur. The presence of alachlor in solution did not affect the rejection of atrazine since no significant difference was detected in the rejection of atrazine spiked as a single solute (36.5%) and in the mixture (35.7%).

Table 4 and Fig. 1 show that the adsorption of atrazine on the membrane is probably the main mechanism governing its rejection because a significant fraction (70% in surface water after sedimentation and 95% in groundwater) of the total percent rejection is due to adsorption on the membrane. Other studies addressing the removal of atrazine using the membranes NF-90 and NF-200 in a cross-flow system showed different rejections and adsorption to the membrane [34,35]. Therefore, it would be interesting to conduct further studies to address and compare the rejections in different natural water matrices using a cross-flow system. This molecule has a lower dipole moment compared to alachlor and therefore, electrostatic interactions are less significant while hydrophobic interactions are predominant. In addition, atrazine is generally the less rejected pesticide studied probably because it has lower molecular weight. Therefore, the rejection of this pesticide appears to result from the combined effect of size exclusion and hydrophobic interactions with a minor contribution from electrostatic interactions. In fact, some studies conducted with atrazine agree with our results and report that the retention of this molecule is governed by a size exclusion mechanism [19], a combined effect of dipole moment, molecular size [11,18], and hydrophobicity [8].

The rejection of alachlor is very dependent on the composition of the water matrix, varying between 17.5% in spring water and 90.4% in laboratory grade water (Fig. 1). The rejections due to adsorption on the membrane, determined for this molecule, are not so significant as for the other compounds filtered (Table 4). The adsorption of this compound in groundwater was not observed and only 31.0% rejection in surface water after sedimentation was related to hydrophobic interactions (being the total rejection 73.6%). The difference in the total rejections reported in groundwater and surface water collected after sedimentation (Fig. 1) could probably be explained by the adsorption observed in the later matrix (Table 4). Besides size exclusion, alachlor rejection appears to be influenced by the ionic composition of the water matrices (Table 2). The alkalinity of the laboratory grade water is very low and then charge effects are significant. Therefore, in laboratory grade water the electrostatic interactions between alachlor and the negatively charged membrane may increase its rejection, which is particularly important because this molecule has a very high dipole moment. In the natural water matrices, the ions present in the water may have a "shielding" effect on the polarized solute and the membrane surface charge, reducing the electrostatic interactions between alachlor and the membrane and then, decreasing the rejection. In fact, in groundwater and spring water that present higher alkalinity (231 and 209 mg/l $CaCO_3$, respectively), the rejections obtained were lower compared to laboratory grade water and surface water after sedimentation. Schäfer et al. [36] also observed the decrease in the rejection of dissolved organic carbon with the increasing ionic strength as a consequence of a "shielding" effect, using ultrafiltration membranes. In addition, the ionic "shielding" of the molecules may also reduce the length of Debye layer of the molecules and therefore, decreasing the rejection by facilitating the breakthrough of the molecules across the membrane [37].

The hardness of the water has been mentioned as a parameter that may influence the retention behaviour of the organic compounds because calcium and magnesium ions may also have an important role in the decrease of repulsive electrostatic interactions, leading to the decrease in the retention. Likewise alkalinity, surface water presents the lowest hardness among the natural water matrices (Table 2). Therefore, the higher rejections are observed in surface water after sedimentation and laboratory grade water, probably because of the higher repulsive electrostatic interactions between alachlor and the membrane in these matrices compared to groundwater and spring water. Boussahel et al. [19] also reported a slight decrease in the rejection of two pesticides in the presence of calcium ions using membrane Desal 5DK. Although other studies addressing the removal of different uncharged organic solutes using different membranes are in agreement with this explanation, the influence of calcium in rejection depends on the membrane type and the ion concentrations [13,16].

Table 4 shows that the total percent rejection observed for pentachlorophenol in Fig. 1 is highly governed by hydrophobic interactions between the compound and the membrane due to the similar total rejection and adsorption percentages determined. However, even though pentachlorophenol is rather hydrophobic, its total percent rejection and percent adsorption were not as significant as the values observed for the PAHs. This behaviour could probably be partly explained since pentachlorophenol is an ionisable organic compound with a pKa value of 4.7 [31]. Its solubility in water is therefore pH dependent and expected to increase at pH values much higher than the pK_a (such as the real water pH values). At pH values of 7 or 8, the dominant species change towards the deprotonated form and the solubility of pentachlorophenol increases [38], decreasing therefore the rejection of this compound compared to the rejections obtained for the PAHs with similar octanol–water partition values. However, other matrix related factors surely play an important role on this compound rejection since different percent rejections were obtained when matrices with similar pH values such as groundwater and spring water were spiked with pentachlorophenol.

The trend obtained for the rejection of pentachlorophenol with the matrix composition is similar to the trend observed for alachlor (Fig. 1 and Table 2). The ionic composition of the water matrices may also influence the rejection of pentachlorophenol since this molecule is deprotonated at the pH of the water sources used. On the other hand, since pentachlorophenol is very hydrophobic, interactions between this molecule and the NOM may also have to be considered. Spring water and surface water (without pre-treatment) are the water matrices that have higher levels of organic matter and the rejections obtained for pentachlorophenol in these two water matrices were the lowest.

The differences in the percent rejections obtained when pentachlorophenol was spiked in the two surface water matrices show that the inclusion of pre-treatment processes prior to nanofiltration would highly increase the membrane process performance in terms of removal of pentachlorophenol, flux decline, and minimization of fouling. In spring water, the inclusion of pre-treatment steps would probably also improve the process performance for the removal of pentachlorophenol and alachlor.

4. Conclusion

Conventional surface water treatment often includes the coagulation, flocculation, and sedimentation processes. In surface and spring water matrices, the nanofiltration process should be placed after these pre-treatments to increase the filtration performance in terms of removal of micropollutants and operation issues (to minimize flux decline and fouling problems).

Nanofiltration has proven to be extremely efficient for the removal of PAHs from real natural water sources with very different compositions. Hydrophobic interactions were found to be the main mechanism governing the rejection of these compounds.

While for the PAHs and atrazine the nanofiltration efficiency may be matrix independent, for many other organic micropollutants, matrix effects can highly impact the efficiency of nanofiltration processes. The results obtained when alachlor and pentachlorophenol were spiked in real water matrices with very different characteristics showed that the removal of these compounds is highly dependent from the matrix composition. The levels and different types of natural organic matter, turbidity, and ionic composition can therefore be expected to impact the removal of defined compounds.

Further research should therefore be conducted to better understand the influence of the different water parameters in the efficiency of the nanofiltration process and how would the membrane process behave in long-term operation after membrane saturation is achieved.

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