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Performance of NF/RO process for indirect potable reuse: interactions between micropollutants, micro-organisms and real MBR permeate

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ABSTRACT

Micropollutants and micro-organisms are major concerns for indirect potable reuse of municipal wastewater. In this study, the retention of pesticides, polycyclic aromatic hydrocarbons (PAHs), metals and micro-organisms in real membrane bioreactor (MBR) permeate matrix and in ultrapure water matrix by nanofiltration (NF) or reverse osmosis (RO) process, and the impact of their retention on NF/RO membrane fouling, were investigated. NF 90 and ESPA2 membranes were chosen for this work. The RO membrane showed high retention for most of the molecules tested, whereas the NF membrane exhibited some variation in the retention of pesticides. The retention of pesticides and metals was enhanced by their interactions with the MBR permeate, while an almost complete retention of PAHs and micro-organisms was observed in both matrices. The presence of PAHs in the MBR permeate increased the permeability of the RO membrane, whereas no such effect was observed for pesticides, metals and micro-organisms. Also, phage leakage was detected when the NF/RO membrane was contaminated by bacteria, which may have caused a slight membrane damage. Pesticide rejection was found to be related to LogKow and molecular weight in ultrapure water at low concentrations (μg/L level).

Keywords: Micropollutants; Micro-organisms; Nanofiltration; Reverse osmosis; MBR permeate; Indirect potable reuse

1. Introduction

Providing an adequate clean water supply is still a serious challenge for many countries around the world today, because of increasing demand, depletion of groundwater, water contamination and drought. In consequence, reclaimed municipal wastewater is now considered as a potential water resource to augment drinking water supplies. While direct potable reuse is rare at this time, indirect potable reuse which involves the blending of highly treated wastewater with natural water resources like groundwater or surface water has been practised in many places. Micro-organisms (bacteria and viruses) and micropollutants, which

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include metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, pharmaceuticals, personal care products, hormones, surfactants etc., are the two main concerns when indirect potable reuse is considered, because of their persistency during conventional wastewater treatment processes and their potential adverse effects on human health [1,2].

The membrane bioreactor (MBR) process is believed to offer a better solution than a conventional activated sludge process in the secondary treatment of wastewater intended for reuse. However, the retention of micropollutants by the MBR process depends on their physicochemical properties and biodegradability, and some micropollutants are only partially removed [3,4]. For example, less than 60% removal of Ni, Pb and As has been noticed in MBRs [5,6]. The retention of PAHs such as fluoranthene and pyrene was shown to be 65 and 58%, respectively, in a submerged MBR designed for nutrient removal [7]. The removal of the pesticide atrazine and the antiepileptic drug carbamazepine was negligible in MBRs [8,9]. Thus, advanced treatments like the nanofiltration (NF)/reverse osmosis (RO) membrane filtration process must be used as a second barrier in indirect potable reuse projects for further retention of micropollutants and micro-organisms, especially when worst-case situations happen in the upstream process, for example when the MBR membrane is damaged.

Many studies have been conducted on the rejection of micropollutants by the NF/RO membrane. Kimura et al. [10] observed that rejection of non-charged compounds was mainly influenced by the size of the compounds, whereas negatively charged compounds could be rejected to a higher extent regardless of the physicochemical properties of the compounds tested, indicating the significant effect of charge repulsion. Nghiem et al. [11] noted that, while oestrogenic hormone retention by more porous membranes decreased with decreasing adsorption, tighter NF and RO membranes could retain oestrogenic hormones effectively. Similar results were obtained by Plakas and Karabelas [12] when studying the retention of herbicides, suggesting the important effects of size exclusion and adsorption. However, Kimura et al. [13] pointed out that the rejection of hydrophobic compounds by NF/RO could be overestimated in short-term experiments where saturation of adsorption sites was not reached. Bellona and Drewes [14] found that increasing feed water pH resulted in an increased negative surface charge, an increased percentage of solutes in the deprotonated state and an increased rejection through electrostatic repulsion. With regard to membrane fouling, it was found that the formation of fouling layer reduced the diffusive transport of solutes across the membrane and increased adsorption capacity of the membrane, thus enhancing the rejection [15,16]. However, Agenson and Urase [17] observed that membrane fouling could result in adsorption and diffusion of solutes across the fouled membrane, which would lead to a marked decrease in the rejection.

Few studies have investigated the retention of micropollutants in real MBR permeates by the NF/RO process. Kimura et al. [18] examined the removal of only six pharmaceuticals in MBR permeates by NF/RO filtration compared to the results in Milli-Q water and found that the presence of organic macromolecules increased the removal of pharmaceuticals by an NF membrane, whereas an RO membrane exhibited very high removal regardless of the presence of organic macromolecules. Comerton et al. [19] investigated the rejection of 22 endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs), spiked into real water matrices including MBR permeate at a dose of approximately 1 μg/L, by NF/RO filtration. The results showed that rejection by the "tight" NF membrane was most strongly correlated with compound LogKow and water solubility with the more hydrophobic compounds showing higher rejection. The RO membrane provided efficient EDC and PhAC removal, whereas the "loose" NF membrane offered poor and variable compound removal. Alturki et al. [20] examined the retention of 40 micropollutants by a combined MBR and NF/RO membrane filtration process and found that the MBR system effectively removed hydrophobic and biodegradable trace organic compounds, while the remaining, mostly hydrophilic, trace organic compounds were shown to be effectively removed by NF/RO membranes.

This study focused on the performance of NF/RO process in the retention of micropollutants and micro-organisms in the real MBR permeate (see Fig. 1). An attempt to bring more practical value to this study was made by adopting the real MBR permeate, using very low concentrations of micropollutants and employing a feed solution containing a blend of many micropollutants. Before the filtration process, micropollutants and micro-organisms were spiked in real MBR permeate or ultrapure water, which was used as a reference to be compared with the real MBR permeate. Thirty-nine micropollutants were selected from three different categories (metals, pesticides and PAHs) and most of them were spiked at the low concentration of 1 μg/L, which is close to the concentration of pesticides and other organic micropollutants observed in the MBR permeate [9]. In addition, most of the micropollutants selected for this study are listed in annex X of the EU water framework directive (EU

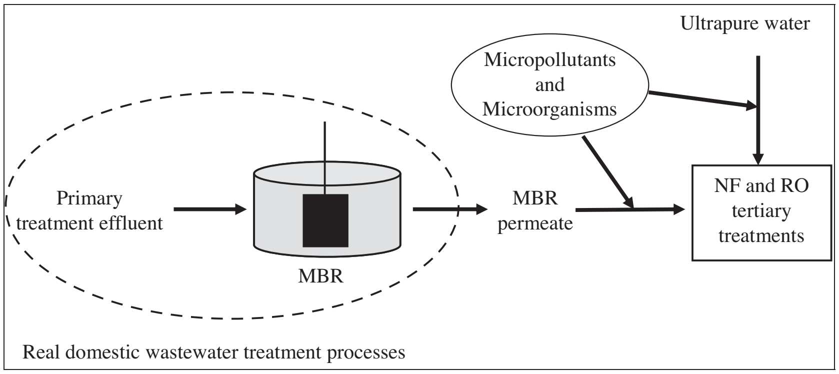

Fig. 1. Processes involved in this study.

WFD). In this study, the effect of interactions between micropollutants, micro-organisms and real MBR permeate on NF/RO retention capacity was investigated. Furthermore, the impact of the presence of micropollutants, micro-organisms and MBR permeate on NF/RO membrane fouling was examined.

2. Materials and methods

2.1. Selected micropollutants and biological hazard indicators

Coliforms and phages are the usual indicators of the removal capacity of a treatment against bacteria and viruses. As the MS2 phage size (about 10–30 nm) is close to that of small human viruses, its use as a biological hazard indicator gives useful information about the filtration efficiency for wastewater reuse.

Metals in urban wastewater are numerous, the most abundant being iron, copper and lead; they are present in the μg/L range. Other metals, such as aluminium, chromium, arsenic, selenium, mercury, cadmium, molybdenum and nickel, are also present in trace concentrations. The metals selected for this study (cadmium, lead, chromium and nickel) are among the most toxic. They are mentioned in the French legislation for water quality control and also in annex X of the EU WFD.

In addition to metals, urban wastewater contains a wide range of organic micropollutants. This study selected five PAHs mentioned in the EU WFD: benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene. Thirty pesticides were also selected from the French legislation and from the EU WFD. They are listed in Table 4 with their molecular weight (MW) and LogKow, which is calculated by SRC's LogKow/KOWWIN Program. LogKow (partition coefficient) is a measure of how hydrophilic (LogKow < 0) or hydrophobic (LogKow > 0) a chemical substance is.

2.2. Analysis methods

2.2.1. Micro-organisms

MS2 (ATCC 15,597-B1) phages were replicated according to the standard procedure (ISO 10,705–1, 1997) using *Salmonella typhimurium* WG49 (NCTC 12,484) as the bacterial host. The sample was centrifuged at 27,000 *g* for 60 min at 4°C (Beckman; model J2–22) and treated with $CHCl_3$. Finally, the viral suspension was stored as stock suspension at 4°C and the final viral concentration was about 10^{11} PFU/mL. The double-layer agar procedure (ISO standard 10705-1,1997) was used to quantify bacteriophage infectious units of MS2 in 10 ml of solution. The results were expressed in PFU/mL.

Total coliforms were detected and counted following the international standard method ISO 9308-1.

2.2.2. Metals

Metals were quantified by an international multi-element method (NF EN ISO 11985) consisting of an acidification of the sample to pH 2 with nitric acid and an analysis by inductively coupled plasma-atomic emission spectroscopy. The wavelengths were 214, 220, 267 and 231 nm for cadmium, lead, chromium and nickel, respectively. The quantification limits were 1 μg/L for chromium and 10 μg/L for other metals.

2.2.3. Polycyclic aromatic hydrocarbons

PAHs were analysed following the international standard method NF EN ISO 17993. Briefly, 500 mL of sample was extracted two times with 50 mL of hexane. The extract was evaporated under a gentle stream of nitrogen and the solvent was changed to methanol in a final 500 μL. The extract was analysed by reversed-phase high-performance liquid chromatography (HPLC)-diode array and fluorimetric detectors. The quantification limit was 10 ng/L for all the PAHs.

2.2.4. Pesticides

The pesticides presented in Table 4 were identified and quantified by an internal method consisting of solid-phase extraction followed by HPLC analysis. Two extractions of 200 mL of sample each were performed on Oasis HLB sorbent at pH 2 and 7 using methanol and dichloromethane as eluants. The extracts were concentrated under a gentle stream of nitrogen and deuterated internal standard was added at a final concentration of 100 µg/L in the 200 µL final volumes of the extract. Then, the extracts were analysed by reversed-phase HPLC followed by electrospray ionisation (ESI)-tandem mass spectrometry. ESI was performed in a positive or negative mode, depending on the compound. Identification and quantification were achieved by multi reaction monitoring. The quantification limit was 20 ng/L for all the compounds.

2.3. NF/RO feed

In this paper, the term "matrix" refers to the composition of the solution before spiking with micropollutants or micro-organisms. The influence of the interactions between micropollutants and the matrix was thus studied by using ultrapure water and MBR permeate matrices. Micro-organisms were injected into mineral water and MBR permeate matrices. Mineral water was used for micro-organisms to prevent cell damage resulting from the contact between micro-organisms and ultrapure water.

The MBR permeate was collected at the domestic wastewater treatment plant of Le Bono (SAUR, France). This full-scale MBR (AquaRM®) contains flat-sheet (Kubota) microfiltration membranes and operates at a hydraulic retention time of 6.5 h, sludge retention time of 17 days and permeate flux of 14 L $m^{-2}h^{-1}$.

The MBR permeate was collected once for all the experiments performed and was analysed according to the analytical methods described in part 2.2. Organic and inorganic micropollutants were below their quantification limit. Neither coliforms nor phage bacterial indicators were detected. The following table (Table 1) lists some other global analyses performed on this effluent. UV, chemical oxygen demand and total organic carbon measurement indicated the organic content of the MBR matrix. Aromatic cycles present maximum absorbance at a wavelength of 254 nm and protein-like substances at 280 nm.

Table 1
Mean MBR permeate characteristics

Indicators	MBR permeate
UV at 254 nm (–)	0.172 ± 0.002
UV at 280 nm (–)	0.137 ± 0.002
COD (mgL^{-1})	15 ± 7
TOC (mgL^{-1})	8.01 ± 0.16
Suspended solids (mgL^{-1})	Below detection limits
Conductivity (μScm^{-1})	685 ± 8

Stock solutions were then made by injecting concentrated micropollutants or micro-organisms into the desired matrix (ultrapure water, mineral water or MBR permeate), so as to obtain a final concentration of micropollutants or micro-organisms as listed in Table 2. Four different spiking solutions were used:

- PAHs (in ultrapure water and MBR permeate).
- Pesticides (in ultrapure water and MBR permeate).
- Cadmium, chromium, nickel and lead (in ultrapure water and MBR permeate).
- MS2 phages and coliforms (in mineral water and MBR permeate).

Stock solutions containing ultrapure or mineral water matrices were then filtered by NF and RO following the protocol as described in part 2.4. Stock solutions containing MBR permeate were filtered by the RO membrane only.

2.4. Filtration protocol

A tight NF membrane (NF90, DOW Filmtec) and a low pressure RO membrane (ESPA2, Hydranautics) were chosen, following Comerton et al. [19] and Jacob et al. [21]. They have shown that loose NF membranes

Table 2
Desired micropollutant and micro-organism concentration in the spiked solution

Micropollutant micro-organism	PAHs	Pesticides	Cadmium	Chromium nickel lead	MS2 Phages	*Coli*
Desired concentration	1 µg/L each	1 µg/L each	50 µg/L	500 µg/L each	2.5×10^8 PFU/mL	2.5×10^5 CFU/mL

Table 3
Membrane characteristics

Membrane	Tight NF	RO
Membrane reference/Manufacturer	NF90/DOW Filmtec	ESPA2/ Hydranautics
Salt retention	85–95% $CaCl_2$>97% $MgSO_4$	>98% $CaCl_2$
Water permeability at 20°C (L/h/m^2/bar) Experimental measurements	9.3 ± 1.2	4.7 ± 0.5
Contact angle (°)	63[a]	69[b]
Zeta potential at pH 6.5 (mV)	Negative −14.2[a]	Negative −7.7[b]

[a] Bellona and Drewes [14], Norberg et al. [22].
[b] Norberg et al. [22].

seem to be less appropriate for the removal of micropollutants due to their poor micropollutant and salt rejection. Table 3 describes the main characteristics of the selected NF and RO membranes. The membrane with the highest salt retention also had the lowest water permeability. Moreover, all these membranes had negative surface charge and tended to be hydrophobic.

A 500-mL (V_0) stirred filtration cell was used for the filtration of the stock solutions (see part 2.3) by RO and NF membranes at constant pressure (8 bars) and constant stirring. Before each filtration, the cell was disinfected with bleach and rinsed with ultrapure water. The permeate outlet pipe was additionally disinfected by means of a Bunsen burner. The velocity of the mixer at the blade extremities was $0.3\,\mathrm{m\,s^{-1}}$. A new $0.0{,}045\,\mathrm{m^2}$ piece of membrane was used for each experiment. Each experiment was repeated three times under the same conditions.

Before filtration, water permeability (Lp_0) was measured. During filtration, the volume of retentate decreased according to the volume of permeate filtered. In order to compare the experiments, the normalized flux (J/J_i) and the volume reduction factor (VRF) (see Eq. (1)) were calculated vs. filtration time. J_i is the initial flux of the clean membrane when it comes into contact with the feed solution. Membrane fouling was then characterized by the plot of J/J_i vs. filtered volume (V_p) or VRF. Filtration experiments took from 1.5 to 2 h for NF and from 3.5 to 4.5 h for RO depending on flux decline intensity.

$$\mathrm{VRF} = \frac{V_0}{V_0 - V_\mathrm{p}} \qquad (1)$$

where V_0 is the initial volume injected into the filtration cell (L), V_p is the volume of permeate filtered (L).

In the case of spiking with micro-organisms, which were the only pollutants of this study that could be compared to particles, the filtration law model described in Eq. (2) was used [23]. Depending on the value of n, fouling mechanisms were identified as follows:

- *Cake filtration ($n = 0$)*: the filter resistance is composed of the membrane resistance and the cake resistance.
- *Intermediate blocking ($n = 1$)*: some particles reaching the membrane participate in the blocking phenomenon by pore sealing and some others just settled on blocked particles.
- *Standard blocking ($n = 1.5$)*: pore volume decreases proportionally to filtered volume by particle deposit on the pore wall.
- *Complete blocking ($n = 2$)*: each particle reaching the membrane participates in the blocking phenomenon by pore sealing.

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \qquad (2)$$

A sample of the stock solution and the full volume of permeate were collected for each experiment and analysed following the analysis protocols described in part 2.2. The retention was then calculated as follows (Eq. (3)).

$$\bar{R} = 1 - \frac{\bar{C_\mathrm{p}}}{C_0} \qquad (3)$$

$\bar{R}$: apparent retention capacity of a given membrane for a given solute.

C_0: solute concentration in the stock solution at $t = 0$ ($\mu\mathrm{g\,L^{-1}}$).

$\bar{C}_p$: average solute concentration in the permeate ($\mu g\, L^{-1}$) calculated according to Eq. (4).

$$\bar{C}_p = \frac{C_{p1} + C_{p2} + C_{p3}}{3} \tag{4}$$

$C_{p1} + C_{p2} + C_{p3}$: Solute concentration in the RO/NF permeate for the 3 filtration repetitions under the same experimental conditions.

3. Results and discussion

3.1. Metal retention

Fig. 2 shows the retention of metals by the NF/RO membrane in two different matrices: ultrapure water and MBR permeate matrices. More than 90% rejection by both NF and RO membranes was observed for all metals tested in ultrapure water matrix. This result concurs with that of Qin et al. [24] who found 94–97% rejection of Ni by an RO membrane in various operating pressure, and at a feed concentration of 21 mg/L, which is much higher than the feed concentration in this study. The retention of metals in ultrapure water matrix by the NF membrane was slightly higher than the result obtained by the RO membrane. This might be explained by the electrostatic adsorption of metal cations on the NF membrane surface, because the surface of the NF membrane chosen (NF90) is more negatively charged than that of the RO membrane (ESPA2) at neutral pH [22]. Moreover, for the RO membrane, higher rejection of all metals was observed in the MBR permeate matrix compared to that in ultrapure water matrix, with permeate concentrations of Cd, Pb and Cr under the detection limit. This might be because metal ions could bind to organic matter, such as humic substances, contained in the MBR permeate [25] and were then retained by the RO membrane together with organic matter. Xu et al. [16] pointed out that the NF/RO membrane became more negatively charged after the membranes were fouled by the microfiltered secondary effluent, which favours the electrostatic adsorption of metal cations on the RO membrane surface.

3.2. Organic micropollutants retention

As regards the retention of PAHs, the permeate concentrations of all PAHs tested were under the detection limit for NF and RO membranes whatever the feed matrix, with the feed concentration being around 1 μg/L for each PAH. Thus, the rejection of all PAHs was estimated to be above 99%. This high retention can be attributed to the adsorption of highly hydrophobic PAHs onto the NF and RO membrane surfaces. A similar result was obtained by Yoon et al. [26], who investigated the retention of 13 PAHs including benzo[a]pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene by NF membrane with a feed concentration below 0.5 μg/L and found that very high retention was achieved.

Fig. 3 and Table 4 show RO and NF retention of 30 pesticides in an ultrapure water matrix. It was found that RO membrane was efficient at removing pesticides, whereas the performance of NF membrane seemed to be more unsteady. For the RO membrane,

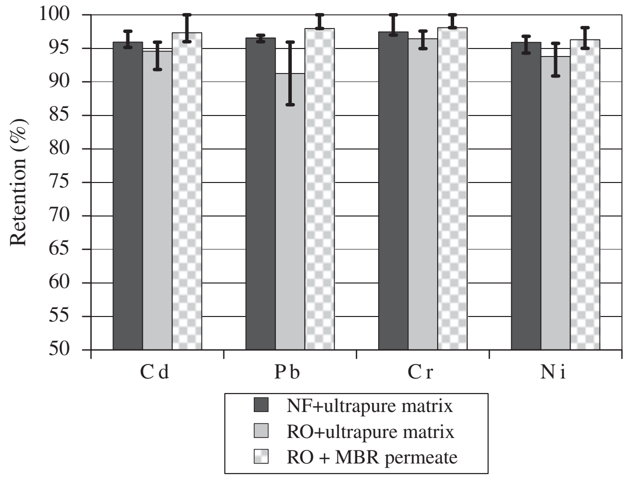

Fig. 2. RO and NF metal retention capacities for ultrapure water and MBR permeate matrices. Feed concentration: 50 μg/L for cadmium, 500 μg/L for lead, chromium and nickel.

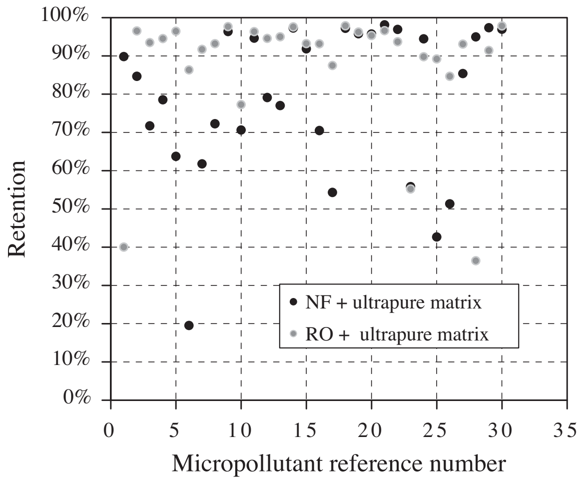

Fig. 3. RO and NF pesticide retention in ultrapure water matrix. Note: Micropollutant reference numbers are listed in Table 4.

Table 4
Characteristics of selected pesticides and their retention by RO/NF depending on the matrix

Ref.	Micropollutant	MW (g/mol)	LogKow*	Ultrapure water matrix				MBR permeate matrix	
				Spiking concentration (ng/L)		Retention (%)		Spiking concentration (ng/L)	Retention (%)
				NF	RO	NF	RO	RO	RO
[1]	Pentachlorophenol	266	4.74	418	505	90	67	1,041	>98
[2]	Atrazine	216	2.82	848	887	85	96	824	>97
[3]	Diuron	233	2.67	1,153	306	72	>93	1,026	>98
[4]	Isoproturon	233	2.84	1,305	520	79	94	926	97
[5]	Simazine	202	2.40	736	960	64	96	777	96
[6]	Carbendazine	191	1.55	826	977	20	86	1,026	97
[7]	Chlortoluron	213	2.58	700	487	62	92	1,026	97
[8]	Cyanazine	241	2.51	869	1,068	78	93	993	97
[9]	Linuron	249	2.91	1,106	854	93	>97	980	>97
[10]	Metamitron	202	1.44	624	661	29	73	851	92
[11]	Metazachlor	278	2.38	1,332	854	96	>96	915	>97
[12]	Methabenzthiazuron	221	2.65	882	165	79	94	995	>97
[13]	Metobromuron	259	2.51	884	510	77	>93	990	>98
[14]	Metolachlor	284	3.24	739	544	>97	>97	915	>97
[15]	Metribuzin	214	1.49	857	664	88	93	1,103	96
[16]	Monolinuron	215	2.26	821	287	68	90	1,058	97
[17]	Monuron	199	2.03	687	640	48	87	860	95
[18]	Neburon	275	4.15	719	930	>97	>97	822	>97
[19]	Norflurazon	303	2.19	785	529	95	>96	1,205	>98
[20]	Propazine	230	3.24	640	426	94	>95	803	>97
[21]	Terbutryn	241	3.77	1,068	585	>98	>96	776	>97
[22]	Terbutylazine	230	3.27	649	317	96	>93	734	>97
[23]	1,3,4-Chlorophenylurea	205	2.00	917	346	56	55	936	88
[24]	Atrazine hydroxy	197	2.09	366	4,048	84	89	457	>95
[25]	Atrazine-desethyl DEA	188	1.78	1,223	730	26.8	89	775	94
[26]	Atrazine-desisopropyl DIA	174	1.39	1,059	599	39	84	736	90
[27]	Terbutylazine-desethyl	202	**	791	612	80	93	733	95
[28]	Terbutylazine-hydroxy	247	**	1,019	218	96	36	736	95
[29]	Diflufenicanil	394	3.53	756	233	>97	>91	1,052	>98
[30]	Epoxiconazole	330	**	658	920	>97	>97	1,027	>98

*From SRC; **Not available.

most of the pesticides were rejected at a rate higher than 90% and only four molecules exhibited a less than 80% rejection. On the other hand, 14 molecules showed less than 80% rejection by the NF membrane. The comparison indicates the significant effect of size exclusion on the retention of pesticides by NF/RO membrane, which is consistent with the results obtained by Plakas and Karabelas [12].

Figs. 4 and 5 show the variation in the retention of the selected pesticides by NF and RO membranes in ultrapure water matrix according to LogKow and MW, respectively. In the figures, an obvious trend can be seen as regards the retention of pesticides by the NF membrane, i.e. the higher the LogKow and MW, the better the retention. In addition, a similar tendency has been noticed for the RO membrane, but it was less obvious, since retention by the RO membrane was high for most of the molecules tested. Nevertheless, this relation was true even for the RO membrane at low feed concentrations and with a blend of pesticides (not one-by-one filtration). Thus, it can explain the low RO rejection of 1,3,4-chlorophenylurea, which has relatively low MW and low LogKow. However, the low rejection of terbutylazine-hydroxy and pentachlorophenol by the RO membrane, 36 and 67%, respectively, could not be explained by the relation mentioned above, considering their relatively high MW or high hydrophobicity (notably the LogKow of pentachlorophenol is 4.74). The reason might be that both terbutylazine-hydroxy and pentachlorophenol contain a hydroxyl group in their chemical structure, and thus tend to be deprotonated at neutral pH and become anions in the water solution, which results in reduced hydrophobicity as explained by Yoon et al. [26]. This assumption is partially confirmed by the fact that rejection of terbutylazine-hydroxy and pentachlorophenol by NF membrane was high in this study, i.e. 96 and 90%, respectively, which might be attributed to the electrostatic repulsion between deprotonated solutes and the relatively highly negatively charged NF membrane surface.

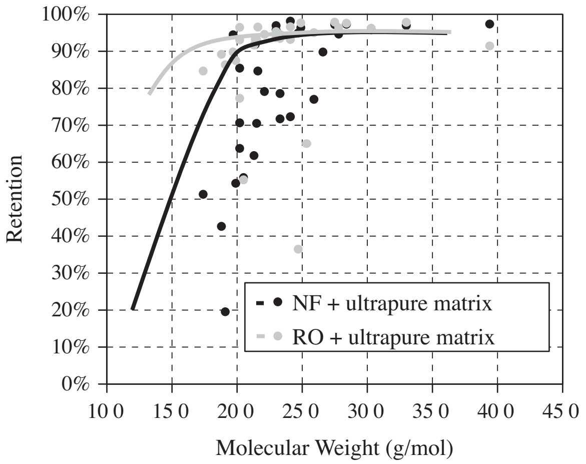

Fig. 5. Variation of NF and RO retention according to micropollutant MW in ultrapure water matrix.

Fig. 6 and Table 4 show the retention of pesticides in the MBR permeate matrix by the RO membrane. It was observed that the presence of MBR permeate increased the retention of almost all pesticides tested, compared to the results obtained in an ultrapure water matrix, and most of the pesticides were rejected at more than 95%, indicating that, in terms of pesticide retention, RO membrane performs better in a real treatment process. Similar results were obtained by Nghiem et al. [11], who observed that the presence of organic matter in solution could enhance the retention

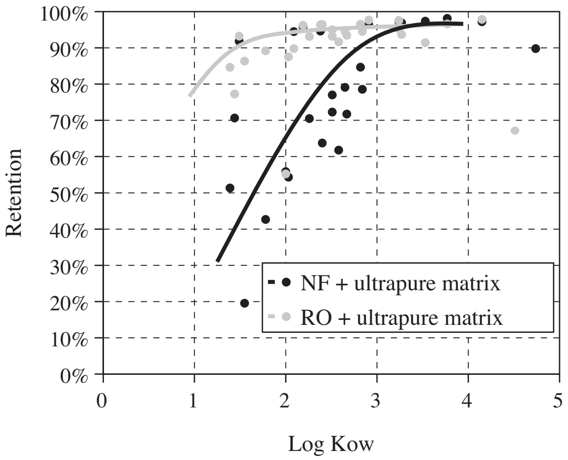

Fig. 4. Variation of NF and RO retention according to micropollutant LogKow in ultrapure water matrix.

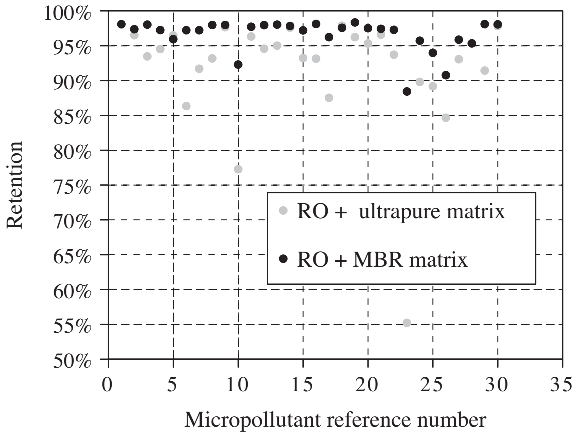

Fig. 6. RO pesticide retention in both MBR permeate and ultrapure water matrices. Note: Micropollutant reference numbers are listed in Table 4.

of oestrogenic hormones by the NF/RO membrane due to the interaction of organic substances with the hormones, which, like pesticides, are hydrophobic compounds. Xu et al. [16] also found that NF/RO membrane fouling caused by filtered secondary effluent could result in an increased adsorption capacity, leading to an increase in the rejection of hydrophobic non-ionic solutes. Moreover, pore restriction caused by organic fouling may enhance the size exclusion effect, thus increasing the retention of pesticides. The significant improvement in retention of pentachlorophenol, 1,3,4-chlorophenylurea and terbutylazine-hydroxy in the presence of MBR matrix confirms the explanations proposed above.

3.3. *Micro-organism retention*

Table 5 shows the average coliphage and coliform retention capacities of NF/RO membrane in mineral water matrix and MBR permeate matrix at transmembrane pressure (TMP) of 8 bars. In terms of coliform retention, no coliform was detected in the NF/RO permeate in any of the situations tested. The complete retention of coliform was expected, since this micro-organism is much bigger than the pore size of the NF/RO membrane. This also partially confirmed the integrity of NF/RO membranes tested. No interference of MBR permeate on coliform retention was observed.

As for MS2 coliphage retention, the results indicated that complete retention (at least 5 log removal for NF membrane and 7 log removal for RO membrane) was obtained in the mineral water matrix, where no interfering flora was found in the permeate. Interfering flora is (non-coliform) bacteria that develop on the analytical media. The same result was observed for the MBR permeate matrix by RO membrane. When the interfering flora was observed in the permeate, a few phages were detected in the NF and RO permeates. Since the experimental apparatus had been previously disinfected, this flora probably came from the membrane itself. Before use, the membrane was packaged in its cartridge and stored dry for 6 months. This storage period may have been prejudicial and membrane contamination may have occurred. Identification of these bacteria by molecular sequencing of rrnB gene, coding for 16S bacterial ribosomal units, gave 98–100% of identification on *Delftia acidovorans*, an aerobic bacterium often identified in water and activated sludge [27], but not present in the RO feed matrix. This bacterium preferentially uses organosulphonates as a carbon source [28], which can explain the presence of the bacteria in the structural layer of NF and RO membranes, where the second layer is made of polysulphone.

Table 5
Micro-organism retention capacities of RO and NF membranes under different conditions (feed concentration, membrane ageing) at 8 bar TMP

Membrane	Feed matrix	Coliform feed concentration (CFU/mL)	Coliform permeate concentration (CFU/mL)	MS2 phage feed concentration (PFU/mL)	MS2 phage permeate concentration (PFU/mL)	Presence of interfering flora
NF	Mineral water	10^3 to 6.00×10^4	0	8.00×10^5	0	no
NF	Mineral water	10^3 to 6.00×10^4	0	8.00×10^5	6–175	yes
RO	Mineral water	1.00×10^7	0	4.30×10^7	0	no
RO	Mineral water	6.00×10^5	0	3.73×10^7	1,540	yes
RO	MBR permeate	5.00×10^6	0	3.45×10^8	3	no

Contaminated membranes were shown to be efficient in trapping coliforms, but exhibited lower coliphage retention. Excluding the hypothesis of cell leaks, which would have meant that coliforms passed, phage leakage could have resulted either from imperfections in the membrane active layer, such as wide pore size distribution or membrane damage caused by *D. acidovorans* micro-organisms. Thus, in the case of the membrane integrity hypothesis, the following mechanism might have occurred. Bacteria might have damaged the active layer producing holes that let coliphages (around 30 nm diameter) go through, but were too small for coliforms (about 1 μm diameter) to pass. According to the Hagen–Poiseuille law, considering the hole as a cylinder of 30 nm diameter and 2 μm length (thickness of the active layer), the flow rate through this hole would be 2.8×10^{-11} $\mathrm{Lh^{-1}}$. This flow rate is negligible compared to the rate resulting from the filtration of 0.0045 $\mathrm{m^2}$ RO membrane, which is equal to 0.15 $\mathrm{Lh^{-1}}$ (average with ultrapure water filtration). Consequently, a few holes of this size would not impact the membrane flux and thus would not be detectable during the experiment.

Because of the need for more experiments and confirmation, these results do not allow definitive conclusions to be drawn, but they stress the need for careful control of all steps of membrane processes, including membrane manufacture, storage and utilization.

3.4. Fouling behaviour of NF and RO membranes according to the matrix and contaminant filtered

Fig. 7 shows the impact of raw and diluted (×2) MBR permeate matrix on RO and NF fouling. Filtration of diluted feed will help towards a better understanding of flux decline mechanisms considering the influence of feed concentration while conserving the composition and the ratios between molecules. The NF flux decline was slightly greater than the RO flux decline when raw MBR matrix was filtered, which is consistent with the results of Ogawa et al. [29]. In contrast, the filtration of diluted matrix underlined the influence of the feed molecule concentrations and interactions with the membrane surface. An increase in concentration can induce a higher molecule flux across the membrane and thus a favourable situation for internal and surface pore blocking. The rise of VRF also causes an increase in polarization concentration at the membrane surface, resulting in a rise of osmotic pressure and consequently a diminution of permeate flux. The latter explanation would better fit the difference of RO flux decline observed in Fig. 7 between diluted and non-diluted MBR permeate filtration. The difference $(1-J/J_i)$ of "MBR permeate" is twice that of "diluted MBR permeate", which is consistent with the dilution ratio. Ultrapure water rinsing, at the end of the filtration, enabled 95% of the RO initial flux to be recovered, which underlined the reversibility of the RO flux decline mechanism. Thus it confirms that the RO flux decline, in that case, was not due to fouling but due to the increase in osmotic pressure according to the VRF.

In contrast to RO, 60−80% of the NF initial flux was recovered, which underlined the presence of organic fouling or internal pore blocking of NF membranes during filtration. This phenomenon has been pointed out in a previous study [21].

Fig. 8 shows the influence of the presence of micro-organisms in mineral water matrix on NF and RO membrane filtration performance. Firstly, it shows a good repeatability of the experimental flux decline.

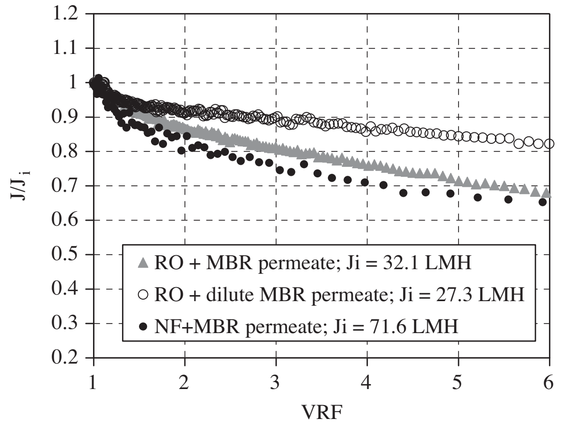

Fig. 7. Impact of raw and dilute (×2) MBR permeate matrix on NF and RO flux decline at 8 bars TMP ($\mathrm{LMH = Lh^{-1}m^{-2}}$).

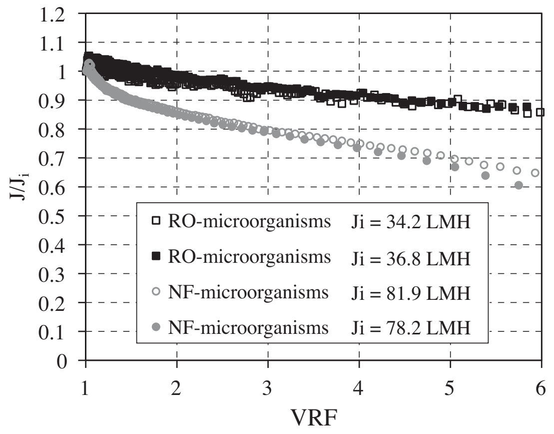

Fig. 8. RO and NF flux decline in the presence of micro-organisms at 8 bars TMP in mineral water matrix.

Secondly, at VRF equal to 6, a 40% flux decline was observed for NF membrane whereas it was 15% for RO membrane in mineral water. Thus, coliforms and MS2 phages, which can be considered as particles of, respectively, 1 μm and 30 nm diameters, probably act as internal or external pore blocking on the NF membrane, gradually decreasing the available filtration surface. Because of their bigger pore size, NF membranes are more prone to pore blocking by MS2 phages than RO membranes, which are considered as dense membranes. The filtration law model (Eq. (2)) using n equal to 1.5 fits the experimental data, which is not the case for RO. This means that pore volume decreases proportionally to the filtered volume because of particle deposit. Consequently, these results agree with our previous MBR permeate filtration results [21], which have shown the predisposition of NF membrane to internal pore blocking.

Fig. 9 shows the RO and NF flux decline in PAH, metal and pesticide filtration. Firstly, flux decline is lower in RO than NF whatever the solutes filtered. Secondly, pesticides seem to have greater impact on membrane fouling than metals and PAHs. Finally, the presence of PAHs increases the permeability of the RO membrane without interfering with PAH retention (see part 3.2). Due to their high hydrophobicity, PAHs could adsorb onto the membrane pore surface and then might cause membrane swelling. Bellona et al. [30] reported that the electrostatic repulsion between the adsorbed solutes within a membrane may result in an increase in pore size of the membrane. For metals and pesticides, the adsorption onto the membrane surface might cause pore restriction, leading to flux decline. The increase in osmotic pressure may also contribute to flux decline.

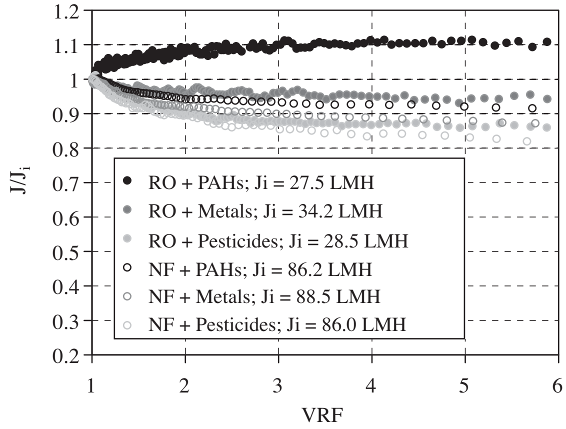

Fig. 9. RO and NF flux decline in the presence of PAHs, Metals and pesticides at 8 bars TMP in ultrapure matrix.

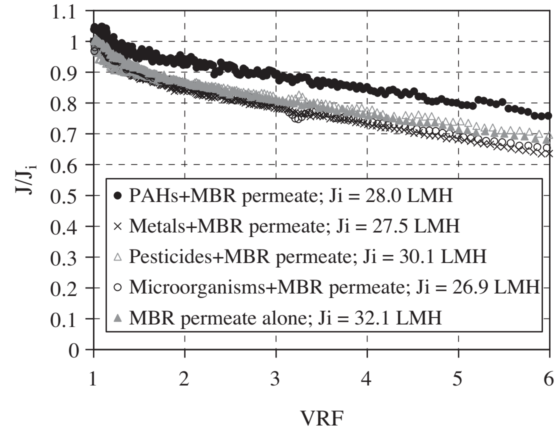

Fig. 10. RO flux decline in the presence of micro-organisms PAHs, metals and pesticides at 8 bars in MBR permeate matrix.

Fig. 10 shows the effect of micro-organisms and micropollutants in MBR permeate on RO membrane fouling. The results indicate that only PAHs seemed to impact membrane fouling by increasing the permeability of the membrane by about 10%. As previously discussed, the adsorption of PAHs on membrane pore surface might result in membrane swelling, which would partially offset the membrane fouling effect caused by the MBR permeate. No impact of micro-organisms and other micropollutants on membrane fouling was observed, indicating that membrane fouling caused by these contaminants was negligible compared to that caused by the MBR permeate. This might be due to the low concentration of contaminants compared to the concentration of foulants in the MBR permeate.

4. Conclusion

The aim of this study was to evaluate the retention of micropollutants and micro-organisms by NF/RO membrane and their fouling potential on NF/RO membrane in MBR permeate and ultrapure water matrices. RO membrane showed high retention of most of the molecules tested, whereas NF membrane exhibited some variation in the retention of pesticides. PAHs and metals were very well retained by both membranes. Pesticide rejection can be related to Log-Kow and the MW of compounds even at low concentrations (few μg/L) and with a mixture of 30 pesticides. The micro-organism retention study underlines the importance of membrane maintenance since bacteria might contaminate the membrane and favour virus permeation. The presence of MBR permeate matrix seems to increase the retention of micropollutants due to the interaction between micropollutants, MBR permeate and NF/RO membrane. In terms of fouling, the selected NF membrane tends to show a higher flux decline than RO membrane at all tested conditions. The presence of PAHs in MBR permeates increased the permeability of RO membrane, while no impact of micro-organisms, pesticides or metals in MBR permeates was observed on the permeability of RO membrane.

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