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Removal of humic acid and chloroform from drinking water by using commercial nanofiltration and reverse osmosis membranes

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ABSTRACT

The removal of disinfection byproducts (DBPs) or their precursors has become an essential step during water treatment processes due to their negative health effects. In this work, the efficiency of commercial nanofiltration (NF) and reverse osmosis (RO) membranes for the removal of chloroform (CF, as the major component of DBPs formed during the chlorination of River Nile water) and humic acid (HA, as the main precursor of DBPs) from drinking water was investigated. Six different commercial membranes were used including NF-90 and NF-270 for NF process and TM-820, SW-30, BW-30 and XLE for RO process. The surface and structural properties of the commercial membranes were characterized using different techniques. From the rejection tests, the whole six membranes removed ca. 100% of HA. In case of CF, NF-90 rejected about 92%, while NF-270 rejected only 76%. The rejection of CF using RO membranes ranged from 94% to 98.5%. CF rejection using the best membranes (SW-30 and BW-30) was tested in a long term filtration experiment (up to 21 h). During this experiment, BW-30 and SW-30 had high rejection efficiency for CF with only a slight decrease in the flux. The current results demonstrate that both SW-30 and BW-30 membranes can be used efficiently to control the DBPs level in drinking water.

Keywords: Humic acid; DBPs; Chloroform; Nanofiltration; Reverse osmosis membranes

1. Introduction

Nowadays, chlorination is the most commonly used chemical disinfection for the purification of drinking water [1]. However, several studies have reported that chlorination of natural organic matter (NOM), such as humic and fulvic acids [2,3] present in fresh water results in the formation of disinfection byproducts (DBPs). These DBPs include trihalomethanes (THMs), haloacetic acids (HAAs) and others. Usually, chloroform (CF) represents the main constituent (42%–58%) of THMs followed by dichlorobromomethane (DCBM) (29%) [4]. Previous studies have demonstrated that THMs may cause liver, kidney or central nervous system problems [5]. Concerns regarding these potential health effects have prompted several countries to develop a number of regulations aiming to reduce and/or eliminate the negative effects of THMs [6]. For instance, the disinfectant/disinfection byproduct regulation in USA has set the maximum contaminant levels for total THMs and HAAs species to be at 80 and 60 µg

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L^{-1}, respectively [7]; while, the WHO guideline for CF is 300 µg L^{-1}. Consequently, removal of the DBPs precursor (i.e., NOM) or the removal of DBPs themselves is an important issue.

Generally, the most common and economically feasible processes for the removal of NOM are the coagulation and flocculation methods followed by sedimentation/flotation and sand filtration [8]. However, these processes have not been proven to completely remove the DBPs. It was revealed in a study, carried out to evaluate the THMs at the outlet of drinking water treatment plants (DWTPs) located in Greater Cairo, Egypt, that THMs are still present at the outlet of the studied plants [9]. This indicates that THMs cannot be removed completely by the currently used traditional treatment process.

In the past, membrane systems were typically used for desalination purposes, however, they are now being used for multiple purposes, including DBPs level control [4,10,11] , pathogen removal, and removal of inorganic and organic chemicals [12]. Different types of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes were tested for the removal of DBPs. The correlation effect of the physico-chemical properties of the membranes and the properties of the feed solutions on the removal efficiency of DBPs has been also investigated [10]. Fouling experiments using humic acid (HA) have been performed as well, but for short time periods (few hours) [13]. All these studies have provided valuable results on understanding the removal processes of these compounds. However, more detailed and focused studies are still needed which would provide a clear picture on the selection of membranes used for efficient removal of DBPs.

The main goal of this study was to assess the rejection of HA (DBPs precursor) and CF (the main component of THMs) using six different commercial NF and RO membranes. The efficiency of the rejection was studied over long operation time using individual or mixed solutions of HA and CF. The used membranes were characterized by several techniques to correlate the rejection and flux results at certain experimental conditions with the structural and surface properties of the membranes.

2. Experimental

2.1. Membrane characterization

Three techniques were used to characterize the membranes including contact angle measurements, zeta-potential measurements and scanning electron microscopy (SEM).

For the contact angle measurements, OCA 15 plus system (Data physics, Germany) was used. Briefly, a droplet of 5 µL of Milli-Q water was delivered onto the dry membrane surface. A static image of the droplet, which in equilibrium with the membrane surface, was taken. Image analysis and contact angle computation were performed using the OCA software. Contact angle measurements were performed for at least 10 times at different locations.

The top surface and cross-section morphology of the membranes were observed by using a Quanta 400 FEG (FEI) environmental SEM at standard high-vacuum conditions. A sputter coater (Emitech, U.K.) was used to coat the outer surface of the sample with a very thin silver film. For cross-section analysis, the membranes were broken using liquid nitrogen. SurPASS electrokinetic analyzer (Anton Paar GmbH) was used for the zeta-potential measurements. In these measurements, the membranes were soaked in 1 mM KCl solution overnight for equilibration before analysis. Streaming potentials of the membranes were measured using 1 mmol L^{-1} KCl solution in 3–10 pH range. Zeta-potential was measured by applying Helmholtz-Smoluchowski equation Eq. (1) [14]:

$$\zeta = (dU/dp) \times (\eta/\in \times \in_o) \times (L/A \times R) \tag{1}$$

where ζ is the zeta potential, dU/dp is the slope of streaming potential vs. pressure , η is the electrolyte viscosity, ε_o is the vacuum permittivity, ε is dielectric constant of the electrolyte, L is length of the streaming channel, A is cross-section of the streaming channel, and R is resistance inside the measuring cell.

2.2. Filtration experiments

Humic acid (sodium salt) (HA), of a molecular range 100–1,000,000 Da, was purchased from Sigma Aldrich (Germany). Chloroform (CF) standard (99.9%) was purchased from SUPELCO. These chemicals were used as received without further purification. Ultrapure water (Milli-Q) was used for the preparation of all solutions used in this study. The commercial NF-90, NF-270, XLE, SW-30, and BW-30 membranes were purchased from DOW-FILMTEC while TM-820 membrane was purchased from TORAY. As indicated by the manufacturer, NF-270 is composed of semi aromatic piperazine-based polyamide layer on top of a polysulfone (PSF) porous support reinforced with a polyester non-woven backing layer. For NF-90, the membrane is fully aromatic polyamide on top of PSF. The RO membranes (TM-820, XLE, SW-30, and BW-30) of the different manufacturers have full aromatic polyamide active layers on top of porous PSF reinforced with a polyester backing.

Prior to the filtration experiments, RO and NF membranes were cleaned in a mixture of ethanol/water for 1 h followed by drying under Argon. The membranes were then re-rinsed 3–4 times in deionized water to ensure complete removal of all organic preservatives. All membranes were subsequently stored in deionized water overnight before using them. The filtration experiments were carried out in a dead-end cell (Fig. 1). The effective membrane area was 9.074×10^{-4} m^2. Volume of the feed solution was 100 mL. All experiments were performed at constant stirring speed of 300 rpm and the feed pressure was maintained at 15 bar using Argon gas. The increase of pressure was done gradually within 30–60 s as indicated by the manufacturer. All membranes were conditioned at the applied pressure for 1–2 h till the conductivity of the permeate reaches 1 µS cm^{-1} to assure removal any residual membranes preservatives and to ensure reaching of Flux steady state through the membranes. Filtration of HA (10 mg L^{-1}), CF (100 µg L^{-1}) and their mixture (of same concentrations) solutions were done at the same experimental conditions. For the long-term experiments, the reloading of the cell was carried out 3 times to perform CF rejection over 21 h.

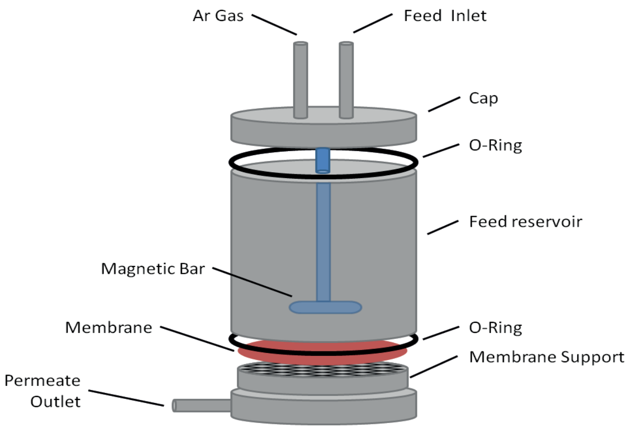

Fig. 1. Schematic diagram of the dead-end filtration cell.

2.3. Analytical methods

Concentration of HA was determined by its UV absorption at the wavelength 254 nm using Cary UV/Vis spectrophotometer according to Standard Method 5910 B [15]. The concentrations of CF and DCBM were measured according to EPA 551 [16] using TRACE GC 2000 system equipped with quadrupole MS detector. All samples were 2 mL in volume and were measured in triplicate to meet QC/QA accordance.

Rejection efficiency using the commercial membranes was calculated as follows:

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \tag{2}$$

where, C_p and C_f are concentrations of model compound in the permeate and in the feed solution, respectively.

3. Results and discussion

3.1. Surface and structural properties of the membranes

The wettability of the membranes plays an important role in determining the membrane performance. For instance, it is mostly agreed in literature that hydrophilic membranes show higher flux and high fouling resistance compared to hydrophobic ones [17]. Table 1 shows the contact angles measured for the six membranes. It is obvious that the membranes have variable values of contact angles due to the different hydrophilic and hydrophobic characters. NF-270, SW-30 and BW-30 showed the lowest values of contact angles (more hydrophilic); while, TM-820 showed the largest contact angle value (the most hydrophobic membrane). NF-90 and XLE were to some extent, less hydrophobic than TM-820.

Table 1
Contact angles (°) of the fresh membranes

Membrane	CA (°) ± SD
NF-90	64 ± 2
NF-270	31 ± 3
TM-820	89 ± 2
XLE	74 ± 4
SW-30	36 ± 3
BW-30	29 ± 2

The zeta potential measurements of the fresh membranes are illustrated in Fig. 2. The measurements were done at different pH values in the range of 3–10. All membranes (except NF-270) showed isoelectric points in the pH range of 4.5–6.5. The positive and the negative zeta potentials were created by the protonation of amine groups and the dissociation of carboxylic groups, respectively [18]. At pH 7, all the studied membranes showed negative value of zeta potential. This behavior could improve the efficiency of these membranes for removing negatively charged organic pollutants from drinking water.

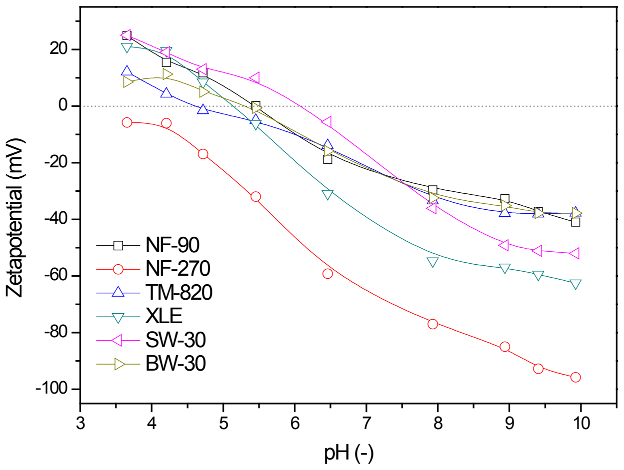

Fig. 2. Zeta potential of the fresh commercial membranes.

Fig. 3 shows the SEM images of the top as well as cross-section views of the studied membranes. All membranes composed of very thin selective layer formed on top of a sponge-like support. The top surfaces of all membranes were rough except for NF-270 and BW-30; their top surfaces were smoother.

3.2. Membrane performance

Different water based solutions were used to measure the permeability of the commercial NF and RO membranes. As shown in Fig. 4, the flux of HA and CF solutions through the six commercial membranes followed the order: NF-270 > NF-90 > XLE > BW-30 > TM-820 > SW-30 supporting that the fluxes of NF membranes are higher than that of RO membranes. For instance, the fluxes of RO membranes ranged from 25 to 105 L.m^{-2}.h^{-1}; while for NF membranes, the flux varied from 100 L.m^{-2}.h^{-1} to 200 L.m^{-2}.h^{-1}. Generally, the highest flux (≈ 200 L.m^{-2}.h^{-1}) was recorded in case of HA filtration on NF-270 membrane. While, the HA and CF fluxes through SW-30 were the lowest (≈ 25 L.m^{-2}.h^{-1}). This

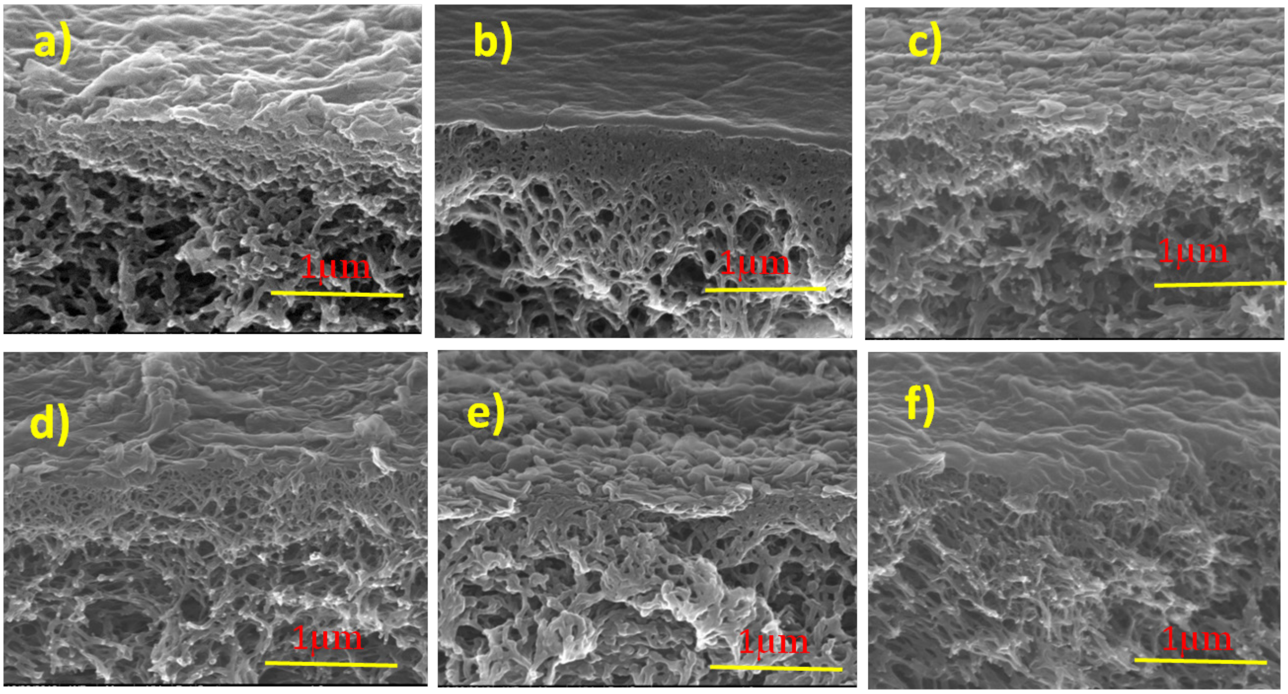

Fig. 3. SEM micrographs of the fresh commercial membranes, (a) NF-90, (b) NF270, (c) TM-820, (d) XLE, (e) SW-30, (f) BW-30.

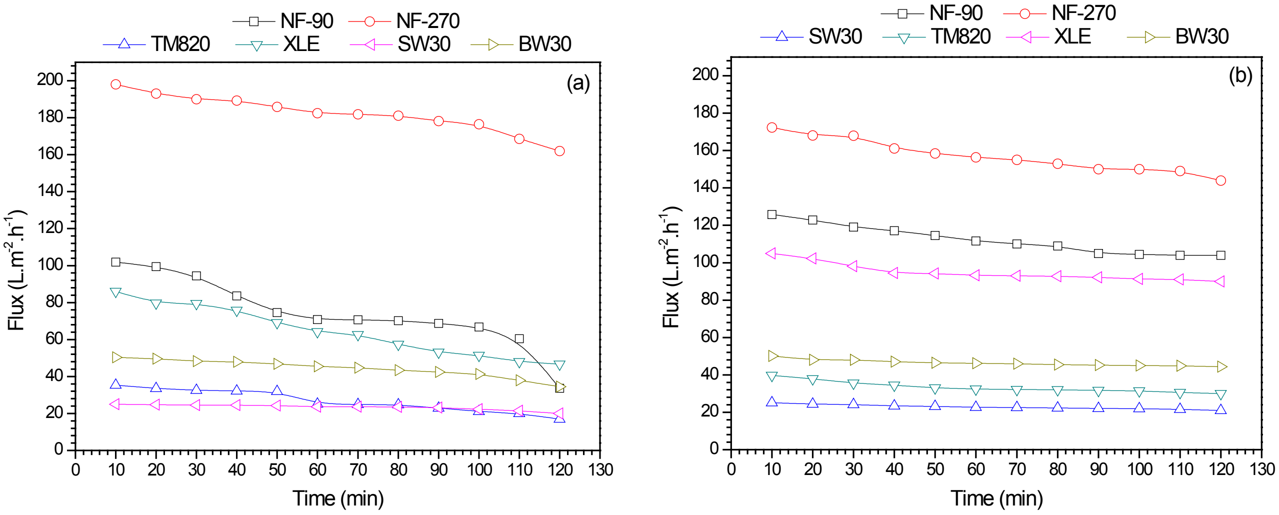

Fig. 4. Evolution of the flux using (a) 10 mg L^{-1} HA and (b) 100 μg L^{-1} CF solutions.

high flux of NF membranes can be attributed to its largest MWCO compared to the other membranes (as indicated in Table 2), and to its high hydrophilicity (low contact angle). The recorded fluxes for NF-270 membrane were in the same range of previously reported data. For instance, the pure water flux through NF-270 membrane was 170 L.m^{-2}.h^{-1} under 20 bar pressure [19], and 70 L.m^{-2}.h^{-1} under 5 bar pressure [20].

It was also revealed that the XLE membrane showed the highest flux among the tested RO membranes which might be due to the lowest roughness for XLE membrane (see Fig. 3.) combined with its relatively high contact angle (i.e., low hydrophilicity).

Table 2
MWCO of the studied membranes (provided by the manufacturers)

Membrane	MWCO (Da)
NF-90	200
NF-270	270–300
TM-820	<100
XLE	<100
SW-30	<100
BW-30	<100

Table 3
Flux decline (ΔJ) during the filtration of HA and CF through the used membranes

Membrane	ΔJ (L.m^{-2}.h^{-1})	
	HA	CF
NF-90	68.3	21.8
NF-270	36	28.3
TM-820	18.4	9.7
XLE	39.3	15.0
SW-30	5.0	4.1
BW-30	15.8	5.7

Table 4
Rejection of the six commercial membranes to different solutions

Membrane	Rejection (%) ± SD	
	HA	CF
NF-90	99 ± 0.5	92.1 ± 1.8
NF-270	98 ± 1	76.1 ± 1.6
TM-820	99.5 ± 0.6	98.5 ± 0.2
XLE	99.5 ± 0.5	94.5 ± 1.6
SW-30	99.5 ± 0.5	97.3 ± 0.3
BW-30	99.5 ± 0.4	97.5 ± 1.3

Additionally, the fluxes of HA and CF solutions through the six membranes decreased with different rates by increasing the filtration time. This is mainly due to the different composition of the active layer of each membrane which reflects different behavior for the flux and the rejection of the pollutants [21].

In order to compare precisely among the changes in flux during the filtration of HA and CF solutions, the flux decline (ΔJ) within the time of experiment (2 h) was calculated using the formula: $\Delta J = J_{10}–J_{120}$, where J_{10} and J_{120} are the fluxes at 10 and 120 min, respectively. The obtained data is presented in Table 3.

The calculated ΔJ reveals that the flux decline during the filtration of HA solution is, in general, more than that of CF. The main reason behind this phenomenon might be the different hyrophobicities of HA and CF. HA is more hydrophobic than CF according to their log K_{OW} values (2.3 for HA and 1.97 for CF) [22]. Since, all studied membranes have hydrophobic moieties as indicated by manufacturers, thereby the adsorption affinity of HA on membrane surface is expected to be higher than that of CF. This easily adsorption will cause higher accumulation of HA on the membrane and more flux decline.

When comparing the performance of NF membranes for HA and CF filtration, it can be noticed that ΔJ is high in the filtration systems HA/NF-90 and CF/NF270. According to the contact angle measurements (Table 1), NF-270 is more hydrophilic than NF-90. Thus, CF accumulation on NF-270 is more favorable than NF-90. This leads to higher ΔJ in case of CF filtration on NF-270 membrane. The reverse is true in case of HA, i.e., HA adsorbs better on NF-90 than NF-270 leading to lower flux in HA/NF-90 filtration system. In addition, the high roughness of NF-90 membranes relative to NF-270 according to the SEM images shown in Fig. 3 might also facilitate the adsorption of HA molecules on the membrane surface [22].

The interpretation of ΔJ data in case of RO membranes was quite difficult. XLE showed the maximum ΔJ value for both HA and CF solutions. This might be due to the high charge present on its surface relative to other RO membranes (see Fig. 2) that caused an interaction between the solute and membrane surface. This explanation might be valid also in case of TM-820. The variable ΔJ of BW-30 and SW-30 may be due to the effect of one or more of the following factors: (1) different surface charge density, (2) variable degree of hydrophilicity and (3) high roughness especially for SW-30.

Regarding the rejection manner, Table 4 shows the rejection efficiency of the membranes to HA and CF solutions. For HA rejection, both NF and RO membranes effectively reject about 100% of HA because of the high molecular weight of humic acid [23] in combination with the low MWCO of the studied NF and RO membranes (as shown in Table 2).

For CF (which is a non-ionic hydrophobic compound) the sequence of CF rejection was: TM-820 > BW-30 ≈ SW-30 > XLE > NF-90 > NF-270; where the rejection ranged from 94% for XLE membrane and 98.5% for TM-820 membrane. Although RO membranes have very low MWCO (as shown in Table 2) which is less than the molecular weight of CF, they did not reject it completely. In fact, the RO membranes do not have well defined pores so part of CF can diffuse in the RO membrane matrix and pass as permeate. In case of NF rejection of CF, rejection ranged from 76% for NF-270 to more than 90% for NF-90. For NF membranes, there are two mechanisms control the removal behavior of organic pollutant; the first one is sieving effect and the second one is the electrostatic interaction [24]. The later mechanism can be excluded due to the nonionic property of CF. Therefore; the differences in the efficiency of CF rejection by NF membranes can be owed to the different MWCOs of NF-270 and NF-90 membranes.

3.3. Long-term rejection of chloroform

In general, Ozaki and Li [24] reported that the rejection of organic solutes by RO membranes depends on the membrane material and solute structure. In addition, it has been documented in other studies that the rejection of solutes by NF/RO membranes is affected by the solute charge (expressed through the acid or base dissociation coefficients, pKa or pKb; of the solute), molecular weight, molecular geometry of the solute, polarity, and hydrophobicity, as well as the membrane surface charge [25].

In our work, only SW-30 and BW-30 membranes were selected to test the rejection of CF over long-time. Where NF-90 and NF-270 were excluded due to their higher MWCO compared to the RO membranes used in this work. Therefore, it was expected that lower rejection values in case of NF membranes will be obtained with respect to the RO membranes. For TM-820 and XLE RO membranes, both showed higher contact angle values which could increase the chance for adsorption of CF (due to increased hydrophobic-hydrophobic interaction; see also Section 3.2) and decrease the rejection.

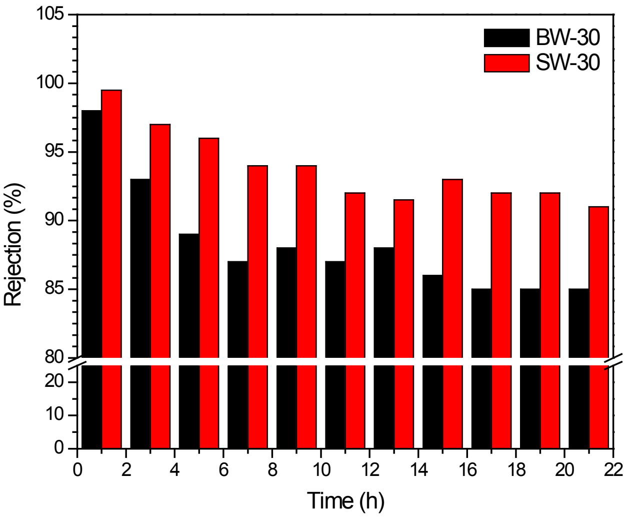

Fig. 5. Rejection of CF over long periods.

The experiments were done continuously over 21 h. As shown in Fig. 5, the highest rejection was obtained during the first hour of operation and then a decline (less than 15%) for both membranes (BW-30 and SW-30) was observed till reaching a steady state after about 7 h. For BW-30, the average rejection of CF was 88 ± 2%; while for SW-30, it was 94 ± 2%. Based on these findings, it is concluded that CF interaction with BW-30 membrane is slightly higher than that with SW-30 membrane. In addition, it is highly recommended to use SW-30 and BW-30 membranes for the rejection of CF. Cleaning the membranes with Milli-Q water was sufficient for the membranes to restore their performance but for sure not up to the initital values (data not shown). The details of the cleaning strategies used will be completed and reported elsewhere.

3.4. Rejection of CF and HA mixture

The main motivation of this step was to study the effect of fouling with HA on CF rejection behavior when using RO membranes. Different CF/HA ratios were used to investigate the effect of the naturally occuring HA in surface water on the rejection efficiency of CF by the studied membranes. By comparing the rejection values for unfouled membranes and membranes fouled with HA, the stable rejection values over 7 h continuous operation was observed as shown in Table 5. The ratio of HA did not change the rejection behavior of BW-30 and SW-30 membranes. This proves that HA fouling on both membranes is not sever. In addition, It is hypothesized that although adsorption can result in initial high rejection, the adsorbed solutes can partition and diffuse across the membranes thus reducing rejection during long-term operation. Size exclusion also played a role in the transport of hydrophobic non-ionic solutes across a membrane.

Table 5
Rejection of CF and HA mixture

Membrane Time (*h*)	TM-820 (50%HA)	TM-820 (70%HA)	SW-30 (30%HA)	SW-30 (70%HA)	BW-30 (70%HA)
1	98.5 ± 0.5	99 ± 0.5	99.5 ± 1	99 ± 1	99 ± 1
3	98 ± 1	99 ± 1	99 ± 0.5	98 ± 0.5	98.5 ± 0.5
5	95 ± 2	98 ± 1	96 ± 2	99 ± 1	98 ± 1
7	95.5 ± 1	98 ± 1	97 ± 1	98.5 ± 1	98 ± 2

4. Conclusions

RO and NF (SW-30, BW-30, XLE, TM-820, NF-270 and NF-90) membranes have been evaluated for the rejection of the harmful disinfection by-products such represented by CF as well as their main precursor (HA). The overall results proved that the used membranes possess high rejection percentages for the studied solutes with different efficiencies. For HA, all membranes could reject up to 100% of initial concentration. While for CF, there was a variable perfromance. Among the six membranes used in this study, SW-30 and BW-30 membranes removed CF effectively at all tested conditions such as: (i) high concentration of the feed solution, (ii) relatively long time of operation (21 h) and (iii) in the presence of HA. However, this issue needs a long term study to investigate the effect of cleaning as a function of time and concentration of the feed solutions.

Based on the excellent removals achieved by commercial NF and RO membranes, it is recommended to combine the low cost conventional treatment with a membrane filtration step to control the DBPs levels in drinking water.

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