



## Sulfate removal from drinking water by commercially available nanofiltration membranes: a parametric study

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### ABSTRACT

The efficacy of nanofiltration (NF) in removing sulfate from a high sulfate content (370–460 mg/L) surface water was investigated. NF tests were carried out using a laboratory-scale cross-flow NF module operated in total-recycle (full-recycle) mode. Membranes of varying characteristics; namely, DK-NF (Desal DK: GE Osmonics, USA), DL-NF (Desal DL: GE Osmonics, USA), and NF270 (Dow Filmtec Co., USA) were tested, and the effects of main operational parameters of cross-flow velocity, trans-membrane pressure, and pretreatment on permeate flux and sulfate removal were evaluated. The NF270 membrane exhibited the highest permeate flux and was found to be the best of the three membranes tested, with over 98% sulfate removal. The DK-NF membrane, which was poor in performance with a high flux decline, provided the lowest sulfate removal, lowest permeate flux, and highest fouling. Microfiltration (2.5- $\mu$ m), as pretreatment, provided no considerable improvement in permeate flux. When the effects of operational parameters on NF performance using the DL-NF membrane were sought, it appeared that permeate flux, and sulfate removal efficiency did not change at all with trans-membrane pressure and cross-flow velocity. The study is expected to provide useful information about the NF of drinking water with high sulfate content in the future.

*Keywords:* Drinking water; Nanofiltration; Sulfate; Operational parameters

### 1. Introduction

Sulfate occurs naturally in numerous minerals, including barite ( $\text{BaSO}_4$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (WHO), and can be formed when sulfide minerals such as pyrite and dolomite are oxidized [1]. Sulfate is also an anthropogenic contaminant. It can be an outcome of several anthropogenic activities such as mining, textile mills, metallurgical refineries, and tanneries, etc. It is a contaminant of concern in surface water or groundwater used as drinking water.

The presence of sulfate in drinking water is known to cause noticeable bitter and medicinal taste. Taste impairment varies with the nature of the counter-ion; taste thresholds have been found to range from 250 mg/L for sodium sulfate to 1,000 mg/L for calcium sulfate [2]. At high concentrations above 1,000–1,200 mg/L, sulfate might cause dehydration, gastrointestinal irritation, and laxative effects in unaccustomed consumers [3]. The WHO Guidelines for Drinking Water Quality proposed no health-based maximum sulfate concentration taking into account the typical

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sulfate levels in drinking water. Nevertheless, the Guidelines recommended the notification of health authorities about the drinking water sources that contain sulfate concentrations above 500 mg/L [2]. The Turkish National Standard on Drinking Water Quality (TS 266), and the USA Secondary Drinking Water Regulation [4] set the sulfate limits of 500 and 250 mg/L, respectively.

Few efforts have been made so far in treating drinking water for the removal of sulfate. These studies have involved traditional technologies such as chemical precipitation [5–7], adsorption [3,7], reduction [8,9], and ion exchange [10]. However, there are many drawbacks to these technologies in water treatment in terms of their applicability, efficiency, and cost. Membrane separation processes that have gained importance in the last two decades are considered to be over these traditional treatment methods. In this context, especially nanofiltration (NF) has appeared as a better choice due to lower operational pressure compared with reverse osmosis (RO) [11–13]. So far, there have been just a few studies towards testing NF membranes in sulfate removal from drinking water. Košutić et al. [14] explored the optimal water treatment process for the removal of sulfate from real water in the location Prud (Croatia) and evaluated the performance of NF. The real water tested had a sulfate concentration of 139 mg/L. They tested two thin-film polyamide NF membranes (NF270 of Filmtec Co., USA and CPA2 of hydranautics) at two different pressures (6.8 and 10 bar). The results of the study showed that both membranes had over 99% sulfate retentions, but the NF270 membrane presented a higher permeation rate than the CPA2 membrane. In a recent study, Jadhav et al. [15] also investigated the removal of sulfate from water by NF. They used the NF270 and NF90 membranes for the removal of multiple contaminants (fluoride, arsenic, sulfate, and nitrate) from ultra-pure water with the spiked mixtures of contaminants. They found both membranes very effective in separating sulfate; the NF90 membrane rejected 95%, whereas the NF270 membrane rejected around 90%, regardless of the operating conditions. They noted that the slightly reduced sulfate rejection of the NF270 membrane was due to its comparably larger pore size. At the expense of lower rejection, the NF270 membrane delivered 1.5 times better flux than the NF90 membrane. Krieg et al. [16] also tested NF90 for sulfate rejection and compared its performance with that of the NF70 membrane from single (NaCl, CaCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>) and binary salt mixtures (NaCl/Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>/CaSO<sub>4</sub>, NaCl/CaCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>/CaSO<sub>4</sub>). The membranes displayed equally effective performance in rejecting sulfate (>90%) and comparable rejection patterns, that is, decreasing rejection with decreasing sulfate concentration.

Although there have been only a few publications on the removal of sulfate from drinking water, several articles have been published on sulfate removal from wastewater. Reis et al. [17] investigated the sulfuric acid plant wastewater treatment using NF and aimed to evaluate the effects of main operational conditions (feed pH, applied pressure, and permeate recovery rate). The membrane used was NF90 (Dow Filmtec, USA), and the wastewater used was real wastewater from a sulfuric acid production plant. When they combined the best operational conditions (feed pH = 2, applied pressure = 10 bar), the NF90 membrane

provided 94% sulfate retention with a recovery rate of only 45%. Another similar study done by Meihong et al. [18] investigated the sulfate removal from the concentrated brine of the chloralkali industry using a thin-film composite (TFC) NF membrane. The researchers showed that sulfate rejection was slightly reduced with increasing feed sulfate concentration and remained above 90% even with a feed concentration above 30 g/L. However, there was a decrease in permeate flux (from 45 to 10 L/m<sup>2</sup> h) with an increase in Na<sub>2</sub>SO<sub>4</sub> concentration (from 10 to 50 g/L). Recently, sulfate removal from an acid solution was investigated by Lopez et al. [19]. They evaluated the performance of NF membranes in treating a synthetic acid solution of Na<sub>2</sub>SO<sub>4</sub> with a sulfate concentration of 9.6 g/L at pHs of 2.0–2.8 and tested NF270 and HydraCoRe 70pHT membranes. The NF270 membrane provided a higher trans-membrane flux and sulfate rejection than the Hydracore 70pHT membrane and allowed to obtain sulfate rejection values over 90%, while HydraCore 70pHT showed rejection values around 75%.

As seen, most of these studies are toward the removal of sulfate from reject streams or mine wastes, or salt spiked pure waters. However, there is no study about the use of NF for the removal of sulfate from high-sulfate surface water. As indicated by Joo and Tansel [20], several factors such as alkalinity, sulfate, total dissolved solids may inhibit the treatment efficiency during NF/RO reject treatment. Therefore, the results from the NF of reject streams or mine wastes, or salt spiked pure waters, cannot be applicable to surface waters. In the present study, NF tests were conducted to assess the performance of NF and the effects of operational parameters such as membrane type, cross-flow velocity (CFV), and transmembrane pressure (TMP) on the performance of different NF membranes in the removal of sulfate from high-sulfate surface water used as a drinking water source. This knowledge is required to identify the operational parameters that can improve sulfate removal in water treatment plants treating high-sulfate waters. We developed a detailed understanding of sulfate removal by NF and investigated different membranes to reduce sulfate levels in the surface water to even lower levels than 250 mg/L in drinking water.

## 2. Experimental setup

### 2.1. Source water

In the experiments, the raw water samples collected from the Kesikköprü Dam Reservoir were used. The samples were collected with bottles of 35 L volume and immediately transferred to the laboratory. Each sample was analyzed for its sulfate, dissolved organic carbon (DOC), turbidity, conductivity, and ultraviolet absorbance at 254 nm (UVA<sub>254</sub>) contents and then kept refrigerated at +4°C. The raw water samples used throughout the experiments had the following characteristics: 370–460 mg/L SO<sub>4</sub><sup>2-</sup>, 3.12–5.03 mg/L DOC, 1.34–1.74 NTU turbidity, 7.5–8.9 pH, 1,350–1,665 µS/cm conductivity and 0.0151–0.0448 cm<sup>-1</sup> UVA<sub>254</sub>.

### 2.2. Filtration tests

The research was carried out mainly in three parts. In the first part, the effect of membrane type was investigated

using three different NF membranes, namely, DK-NF (Desal DK: GE Osmonics, USA), DL-NF (Desal DL: GE Osmonics, USA), and NF270 (Filmtec Co., USA) (Table 1). In the second part of the study, the effect of microfiltration (MF) pretreatment on the NF of sulfate was studied. In the third part, a parametric study was conducted in which the effects of CFV and transmembrane pressure (TMP) were investigated (Table 2).

In NF tests, a lab-scale cross-flow type system (SEPA CF II Membrane Element Cell, Italy) in which a single piece of the rectangular membrane was used as the filtration unit. Tests were conducted in total recycle mode in which both permeate and concentrate streams are returned to the feed

tank so that the characteristics of the feed water are kept constant (Fig. 1). The temperature of the filtration system was kept constant at  $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$  during the experiments by cooling with tap water. The membranes used in the experiments are flat sheet type membranes with an effective area of  $140\text{ cm}^2$ . The NF tests lasted 8 to 15 h depending on the time needed for the steady-state, which was checked by measuring the permeate flux. Permeate samples were collected in specific periods and analyzed for their sulfate content, temperature, conductivity, and  $\text{UVA}_{254}$  levels. In the experiments carried out to investigate the effect of pretreatment on the fouling of downstream NF membranes, dead-end MF experiments were run using a conventional

Table 1

Characteristics of the membranes (the numbers in square brackets indicate the reference number)

	DK-NF	DL-NF	NF270
Manufacturer	GE Osmonics, (USA)	GE Osmonics, (USA)	Dow Filmtec, (USA)
Polymer structure	Thin-film polyamide [22]	Thin-film polyamide [22]	Thin-film polyamide [25]
pH range	2–10	2–10	2–11
MWCO (Da)	~150–300	~150–300	~200–400
	150 [23]	300 [23]	150–200 [25]
	230 [24]	340 [24]	
Pore radius (nm)	0.43 [26]	0.46 [26]	0.43 [23,27] 0.34 [28]
Rejection (% $\text{MgSO}_4$ )	96	98	99.2
Zeta potential at pH 7.9 (mV)	$-27 \pm 2$ [29]	$-24 \pm 1$ [29]	$-28 \pm 1$ [29]
Contact angle	$37 \pm 4$ [29]	$31 \pm 3$ [29]	$30 \pm 3$ [29]
Isoelectric point	2.08 [24]	2.71 [24]	5.2 [22]
	3–4 [30]		
Charge (at pH above isoelectric point)	Negative	Negative	Negative

Table 2

Experimental matrix

Experiment	Membrane type	TMP (bar)	CFV (m/s)	2.5 $\mu\text{m}$ MF pretreatment
Effect of membrane type				
1	DK-NF	6.9	1.2	No
2	NF270	6.9	1.2	No
3	DL-NF	6.9	1.2	No
Effect of pretreatment				
2	NF270	6.9	1.2	No
4	NF270	6.9	1.2	Yes
3	DL-NF	6.9	1.2	No
5	DL-NF	6.9	1.2	Yes
Effect of CFV				
6	DL-NF	6.9	0.7	Yes
5	DL-NF	6.9	1.2	Yes
Effect of TMP				
7	DL-NF	3.5	1.2	Yes
5	DL-NF	6.9	1.2	Yes

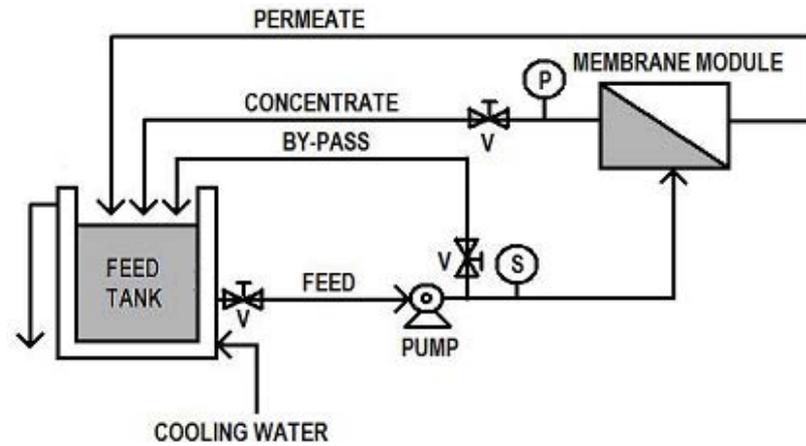


Fig. 1. Total recycle mode flow diagram (V: valve; P: pressure gauge; S: suction gauge).

vacuum filtration apparatus (Millipore, Germany) and 2.5 μm membranes (Whatman 42) with an effective area of 14 cm<sup>2</sup>.

The performance of NF was assessed in terms of % solute rejection (*R*) and permeate flux (*J*). *R* is calculated as:

$$R = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \quad (1)$$

where *C<sub>p</sub>* and *C<sub>f</sub>* are the concentration of the species in the permeate and feed streams, respectively, with the unit mg/L.

Permeate flux (*J*) in L/m<sup>2</sup> h was calculated as:

$$J = \frac{V_p}{A_m \times t} \quad (2)$$

where *V<sub>p</sub>* is the permeate volume in L, *t* is time in h, and *A<sub>m</sub>* is the effective membrane area in m<sup>2</sup>.

Water permeance (*P*) in L/m<sup>2</sup> h bar was obtained by the following expression:

$$P = \frac{J}{TMP} \quad (3)$$

where TMP is the transmembrane pressure in the bar.

### 2.3. Membrane preparation and cleaning

All the membranes used in the NF tests were compacted at 13.8 bar for 24 h to prevent possible expansion and contraction of the pores of the membrane during experimental runs passing double distilled water (DDW). After compaction, the membranes were chemically cleaned by applying a clean-in-place method. The membranes were exposed to HNO<sub>3</sub> at pH 3 for 30 min, followed by NaOH at pH 9–10 for 30 min while they were in the module [31,32]. DDW was passed through the system before and after the raw water was fed into the system. DDW and raw water fluxes were measured until the system reaches steady-state at the desired experimental TMP and CFV.

### 2.4. Flux decline calculations

The flux declines were calculated, and the extents of concentration polarization and fouling were assessed using the equations given in Table 3. The flux measurements were performed in four steps:

- *Initial clean water flux (J<sub>cwi</sub>)*: The clean (pure) water flux was determined with the clean membrane, which was subjected to the initial chemical cleaning and compaction.
- *Raw water flux (J<sub>rw</sub>)*: The raw water flux stabilized with respect to time during raw water filtration.
- *Clean water flux of the fouled membrane (J<sub>cwf</sub>)*: The clean water flux is measured with the fouled membrane after the raw water filtration.
- *Clean water flux of the chemically cleaned membrane (J<sub>cwc</sub>)*: The clean water flux is measured with the cleaned membrane after the cleaning procedure [31].

In addition to the flux decline values, fouling resistances (*R<sub>f</sub>*) of the membranes were calculated using Darcy's Law:

$$P = \frac{1}{\mu \times R_{tot}} \quad (4)$$

where *P* is the permeance (L/m<sup>2</sup> h bar), μ is the permeate viscosity (Pa.s), and *R<sub>tot</sub>* is the total flow resistance on the membrane (m<sup>-1</sup>) which is equal to:

$$R_{tot} = R_f + R_m \quad (5)$$

where *R<sub>m</sub>* is the intrinsic membrane resistance to the flow (m<sup>-1</sup>), and *R<sub>f</sub>* is the fouling resistance of the membrane (m<sup>-1</sup>).

*R<sub>m</sub>* was calculated using the Eq. (6):

$$P_{cwi} = \frac{1}{\mu \times R_m} \quad (6)$$

where *P<sub>cwi</sub>* is clean water permeance. The fouling resistance (*R<sub>f</sub>*) of the membranes was then calculated by substituting *R<sub>tot</sub>* and *R<sub>m</sub>* into Eq. (5).

Table 3  
Flux decline analysis

Calculation	Explanation
$(J_{cwi} - J_{rw}) / J_{cwi}$	Total flux decline
$(J_{cwi} - J_{cwf}) / J_{cwi}$	Flux decline due to fouling (irreversible + reversible)
$(J_{cwf} - J_{rw}) / J_{cwf}$	Flux decline due to external fouling associated with concentration polarization
$(J_{cwi} - J_{cwc}) / J_{cwi}$	Flux decline due to irreversible fouling

### 2.5. Analytical methods

Sulfate concentration was measured by a Hach DR-2000 spectrophotometer (USA) according to the USEPA-approved Hach Method No. 8051 (equivalent to USEPA method 375.4). UV absorbance at 254 nm ( $UV_{254}$ ) was analyzed with a Varian 100 Spectrophotometer (The Netherlands). This method was adapted from Standard Methods for the Examination of Water and Wastewater [33]. Conductivity, pH, and total dissolved solids were measured directly by using a Hach Sension 378 Instrument (USA). Turbidity measurements were done using a Hach 2100N model turbidimeter (USA). For the analysis of DOC, a TOC-5000A analyzer (Shimadzu, Japan) applying a high-temperature combustion method [33] was used.

### 3. Results and discussion

In the following sections, the results obtained throughout the experiments are presented and discussed.

#### 3.1. Comparison of different NF membranes

As the first trial, the DK-NF membrane was employed, and its performance in the removal of sulfate was examined. Two parallel tests were conducted at 6.9 bar TMP and 1.2 m/s CFV using the same membrane specimen. The sulfate level of the raw water fed to the system in the first and second tests were 460 and 400 mg/L, respectively (Fig. 2). In the first test, after the 10th hour, the sulfate removal was steady with a permeate sulfate concentration of 75 mg/L that corresponds to a sulfate removal of about 79.7% (Fig. 2a). In the second test, the reduction in permeate sulfate concentration showed a similar trend with 84.3% sulfate rejection at steady-state. Meanwhile, in both the tests, there was a complete removal of organic matter from the raw water as indicated by the  $UV_{254}$  absorbance values (Table 4). In contrast to  $UVA_{254}$ , the conductivity reduction was by 83.7%, which was in accordance with the sulfate removal.

As the sulfate removal of the DK-NF membrane was found to be low, the NF270 and DL-NF membranes were tested, and the sulfate rejection performances indicated in Figs. 2b and c were observed. As seen, there was a sharp decrease in the permeate sulfate concentration within the first hour of filtration for these two membranes. The average steady-state sulfate rejection with the NF270 membrane was 98.3%, with a permeate sulfate concentration of 7.5 mg/L. The DL-NF membrane exhibited almost the same performance with a rejection of 98.5%, which corresponds to the permeate concentration of 3.5 mg/L (Table 4). These findings are in accordance with the sulfate rejection reported by Košutić et al. [14] who tested the NF270 and CPA2

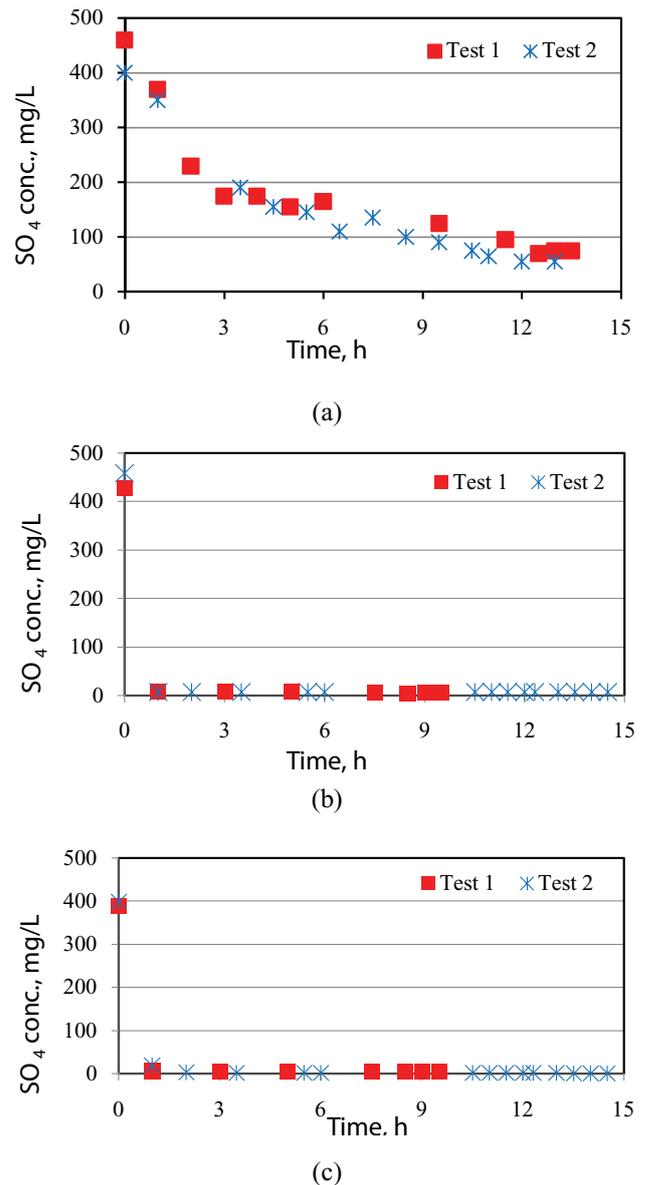


Fig. 2. Time-dependent sulfate concentration in permeate; (a) DK-NF, (b) NF270 and (c) DL-NF (CFV = 1.2 m/s, TMP = 6.9 bar, no pretreatment).

membranes and achieved a sulfate rejection of 99% for a surface water-bearing 139 mg/L sulfate.

Almost equal and significant sulfate rejection by the NF270 and DL-NF membranes, which was much higher

Table 4  
Performances of the DK-NF, NF270 and DL-NF membranes (TMP = 6.9 bar; CFV = 1.2 m/s)

		Permeate flux (L/m <sup>2</sup> h)	Permeate sulfate (mg/L)	Reduction in sulfate (%)	Reduction in conductivity (%)	Reduction in UVA <sub>254</sub> (%)
DK-NF	Test 1	33.3	75.0	79.7	83.3	100
	Test 2	34.0	55.0	84.3	84.1	100
	Average	33.7 ± 0.5	65.0 ± 14.1	82.0 ± 3.3	83.7 ± 0.6	100 ± 0
NF270	Test 1	87.5	7.0	98.4	65.6	100
	Test 2	85.7	8.0	98.2	65.6	100
	Average	86.6 ± 1.3	7.5 ± 0.7	98.3 ± 0.1	65.6 ± 0.0	100 ± 0
DL-NF	Test 1	67.0	2.0	98.6	59.9	100
	Test 2	32.6	5.0	98.4	54.4	79
	Average	49.8 ± 24.3	3.5 ± 0.7	98.5 ± 0.1	57.2 ± 3.9	90 ± 14.8

than that by the DK-NF membrane, indicated that the rejection of sulfate is not only by the pore size exclusion mechanism. The other separation mechanisms, such as adsorption onto the membrane surface, adsorption onto particles in the cake layer, or sieving as a result of physical constriction of the membrane pores due to fouling, were thought to be effective as indicated by several other investigators [34–37]. As shown in Table 1, the pore radius of all membranes tested is almost the same, so pore size exclusion would not be the only mechanism in sulfate rejection.

Although these two membranes provided similar permeate sulfate levels, the permeate fluxes were different. The NF270 membrane provided a much higher permeate flux than the DK-NF membrane. The average permeate flux attained with the DL-NF membrane was about 49.8 L/m<sup>2</sup> h while it was 86.6 L/m<sup>2</sup> h with the NF270 membrane. On the other hand, the conductivity and UVA<sub>254</sub> removals by the NF270 were considerably higher than those by the DL-NF membrane. Based on these results, the NF270 membrane appeared as outperforming.

As can be seen from Table 4, a complete organic matter rejection was evident from 100% UVA<sub>254</sub> reduction observed with the DK-NF and NF270 membranes. This finding indicated that these two membranes preferentially removed aromatic/hydrophobic organics to which UVA<sub>254</sub> is attributed. Similar findings were reported by Ates et al. [36], Amy and Cho [38], and Rubia et al. [39]. Ates et al. [36] reported different natural organic matter removal efficiencies with different membranes and attributed the differences to the MWCOs of the membranes. In the present study, the DL-NF membrane provided the lowest steady-state UVA<sub>254</sub> rejection of about 90%. This result was expected because the nominal MWCO of the DL-NF membrane is higher than that of the NF270 and DK-NF membranes. It should be noted that the tests were carried out with the same surface water having the same ionic concentration, and all three membranes possess similar zeta potentials (Table 1). Assuming that the possible alterations in the zeta potentials of all three membranes due to the actual pH and ionic strength of the surface water will almost be the same, one should not expect to have more/less swollen matrix resulting in a lower/higher pronounced effects of zeta potential on membrane MWCO and in turn UVA<sub>254</sub> rejection [30].

Another possible reason for low organic matter retention by the DL-NF membrane was speculated as the presence of low molecular weight natural organics in the surface water. Ates et al. [36] reported a lower removal of low molecular weight organics (i.e., <2,000 Da) with the DL-NF than with the DK-NF membrane.

Membrane fouling is an important operational challenge that results in membrane permeability impairment and increased operating costs [40]. Therefore, for a better comparison of the three membranes, their clogging behaviors were compared. As presented in Table 5, the permeate flux from the DK-NF membrane (33.7 L/m<sup>2</sup> h) was about 60% lower than that of the NF270 membrane (86.6 L/m<sup>2</sup> h), and 30% lower than that of the DL-NF membrane (49.8 L/m<sup>2</sup> h). From Table 5, it is also seen that the highest total flux decline (25.8%) was with the DK-NF, followed by the NF270 membrane (11.8%) and the DL-NF membrane (2.6%). The flux decline due to concentration polarization was also higher for the DK-NF membrane (22.0%) than for the other two membranes. All these findings for the DK-NF membrane indicated that the flux decline for this membrane originated primarily from concentration polarization and was mostly irreversible. The flux decline due to fouling was only 4.7% for this membrane. Similar to the DK-NF; the flux decline due to fouling of the NF270 membrane was only 4.4%, and the flux decline was mostly due to concentration polarization. However, the flux decline due to irreversible fouling of the NF270 membrane (4.7%) was much lower than that of the DK-NF membrane (24.4%). In terms of irreversible fouling, the DL-NF membrane was superior to the other two membranes with no irreversible fouling. These findings indicated that chemical cleaning provides an excellent flux recovery for the DL-NF and NF270 membranes, but especially for the DL-NF membrane.

Given the low flux and high flux decline with the DK-NF membrane, it was decided to exclude this membrane and continue the experimental studies with the DL-NF and NF270 membranes.

### 3.2. Effect of pretreatment

In the NF of surface water, dissolved inorganic or organic compounds, colloidal particles, bacteria, or suspended

solids may cause fouling and, therefore, can lower the permeate flux. The decrease in permeate flux can be reversible or irreversible. Tahri et al. [41] used electrostatic repulsion and attraction to explain the flux decline due to the fouling phenomenon and considered the integration of MF as a pretreatment to NF to prevent obstruction and damage of the membrane and reduce the effect of fouling.

In the present study, MF with a 2.5 μm pore size membrane was employed as a pretreatment to NF in dead-end filtration mode, and the results presented in Table 6 were obtained. As expected, MF of the raw water provided only a slight sulfate (4.8% to 11.5%) and conductivity (16.6%) retention. When this micro-filtered raw water was used as a feed to the NF270 and DL-NF membranes, the MF pretreatment was found not to affect NF performance seriously (Table 6). The sulfate, conductivity, and UVA<sub>254</sub> retention efficiencies obtained with both NF membranes after MF were comparable to those without MF. However, the application of MF before the NF270 membrane provided a slight improvement in the sulfate reduction from 98.2% to 99.2%. Water flux, flux decline, and fouling characteristics are presented in Table 7 for the NF experiments conducted with and without MF. In the case of the NF270 membrane, without MF, the total loss of permeate flux was recorded as 11.8%. This flux decline was improved to only 9.6% with the application of MF, which was indeed not a considerable improvement. Fouling was found to be partly reversible. The NF process with the 2.5 μm prefiltration was not subjected to fouling. Thus, a very slight positive effect of the 2.5 μm MF before NF270 was seen in this respect. Similarly, when MF was applied as pretreatment for the DL-NF membrane, there were no considerable effects on the fouling characteristics. This observation is in agreement with Kim et al. [42] who indicated that MF pretreatment did not decrease the fouling tendency of the UTC-70 membrane, and a higher level of pretreatment might lead to a higher initial flux, which in turn might cause the poor overall performance of membranes.

As presented above, although the two membranes had almost the same sulfate removal performance, the DL-NF membrane had a lower raw water flux. Therefore, further experiments on the effect of TMP and CFV were conducted with the DL-NF membrane to investigate the possible improvement in its performance.

3.3. Effect of cross-flow velocity

The phenomenon of concentration polarization, which affects the flux, retention, and fouling of the membrane, is the major drawback of the NF process. It is caused by the accumulation of retained solutes near the membrane on the high-pressure side. As the concentration of solutes at the membrane surface increases, a boundary layer forms as a result of the equilibrium between the convective solute transport towards the membrane and the back diffusion of the retained species [43]. There is a close relationship between concentration polarization and CFV. Increased CFV increases the shear force that causes a decrease in the polarization layer. This decrease in polarization level increases the permeate flow.

To investigate the effect of CFV on sulfate removal, the system was fed with pre-filtered surface water, and NF

Table 5 Water flux, flux decline and total fouling for the membranes (TMP = 6.9 bar; CFV = 1.2 m/s)

	Permeate flux (L/m <sup>2</sup> h)			Raw water	Total	Flux decline (%)		
	Clean water	Raw water				Due to fouling	Due to concentration polarization	Due to irreversible fouling
	$J_{cwi}$	$J_{cwf}$	$J_{cwc}$	$J_{rw}$	$(J_{cwi} - J_{rw})/J_{cwi}$	$(J_{cwf} - J_{rw})/J_{cwf}$	$(J_{cwi} - J_{cwf})/J_{cwi}$	$(J_{cwi} - J_{cwc})/J_{cwi}$
DK-NF	Test 1	40.4	38	33.3	17.6	5.9	12.4	14.6
	Test 2	51.6	49.8	34	34.1	3.5	31.7	34.1
	Average	46.0 ± 7.9	43.9 ± 8.3	34.3 ± 0.4	33.7 ± 0.5	4.7 ± 1.7	22.0 ± 13.7	24.4 ± 13.8
NF270	Test 1	99.7	97.4	96.7	12.2	2.3	10.2	3
	Test 2	96.7	90.5	90.5	11.4	6.4	5.3	6.4
	Average	98.2 ± 2.1	94.0 ± 4.9	93.6 ± 4.4	86.6 ± 1.3	4.4 ± 2.9	7.8 ± 3.5	4.7 ± 2.4
DL-NF	Test 1	69.5	70.6	70.3	3.6	None	5.1	None
	Test 2	33.1	37.5	39.3	1.5	None	13.1	None
	Average	51.3 ± 25.7	54.1 ± 23.4	54.8 ± 21.9	49.8 ± 24.3	None	9.1 ± 5.7	None

Table 6  
Effect of 2.5 µm MF on the characteristics of the permeate from the NF270 and DL-NF membranes (TMP = 6.9 bar; CFV = 1.2 m/s)

	Normalized flux $J_{rw}/J_{cwi}$	Sulfate (mg/L)		% Removal		Conductivity (µS/cm)		% Removal		UVA <sub>254</sub>		% Removal
		Average		Average		Average		Average		Average		
		Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	
DL-NF												
Raw water		430.0	440.0	435.0 ± 7.1		1,651	1,634	1,643 ± 12		0.0166	0.0406	0.0286 ± 0.0170
2.5 µm		400.0	370.0	385.0 ± 21.2	11.5	1,389	1,350	1,370 ± 28	16.6	0.0294	0.0286	0.0290 ± 0.0006
DL-NF	0.97	2.0	5.0	3.5 ± 0.7	99.2	678	724	701 ± 33	57.3	0	0.0072	0.0030 ± 0.0051
2.5 µm + DL-NF	0.90	6.0	7.0	6.5 ± 0.7	98.5	654	745	700 ± 64	57.4	0	0.0063	0.0032 ± 0.0045
NF270												
Raw water		430.0	410.0	420.0 ± 14		1,651	1,545	1,598 ± 75		0.0166	0.0556	0.0361 ± 0.0276
2.5 µm		400.0	-	400.0	4.8	1,618	-	1,618		0.0225	-	0.0225
NF270	0.88	7.0	8.0	7.5 ± 0.7	98.2	573	573	573 ± 0	64.1	0	0	0
2.5 µm + NF270	0.90	3.0	-	3.0	99.2	555	-	555	65.3	0	-	0

Table 7  
Effect of MF on the performances of NF270 and DL-NF membranes (TMP = 6.9 bar; CFV = 1.2 m/s)

	Permeate flux (L/m <sup>2</sup> h)						Flux decline (%)					
	Clean water		Raw water		Total flux decline		Due to concentration polarization		Due to fouling		Due to irreversible fouling	
	$J_{cwi}$	$J_{cwf}$	$J_{cwc}$	$J_{rw}$	$(J_{cwi} - J_{rw})/J_{cwi}$	$(J_{cwi} - J_{rw})/J_{cwi}$	$(J_{cwi} - J_{rw})/J_{cwi}$	$(J_{cwi} - J_{cwf})/J_{cwi}$	$(J_{cwi} - J_{cwf})/J_{cwi}$	$(J_{cwi} - J_{cwc})/J_{cwi}$	$(J_{cwi} - J_{cwc})/J_{cwi}$	
NF270	98.2	94.0	93.6	86.6	11.8	7.8	4.3	4.7	4.7	4.7	4.7	
MF + NF270	84.6	85.1	94.1	76.5	9.6	10.1	None	None	None	None	None	
DL-NF	51.3	54.1	54.8	49.8	2.9	7.9	None	None	None	None	None	
MF + DL-NF	57.2	55.0	56.7	51.6	9.8	6.2	3.8	0.9	0.9	0.9	0.9	

performance was monitored using the DL-NF membrane at two different CFVs. As presented in Fig. 3, decreasing the CFV from 1.2 to 0.7 m/s did not have any effect on steady-state sulfate and conductivity retentions. However, UVA<sub>254</sub> retention increased to 100% from its earlier value of 80.7%. The improvement observed in the removal of UVA<sub>254</sub> causing substances was attributed to the possible sorption of UVA<sub>254</sub> causing organic matter onto the membrane surface and also particulate matter accumulated there [44].

As can be depicted from Table 8, when CFV was increased from 0.7 to 1.2 m/s, there was almost no change in the normalized raw water permeate flux ( $J_{rw}/J_{cwi}$ ). The normalized flux decreased from 0.98 to 0.90 when the CFV increased from 0.7 to 1.2 m/s. However, this was not considered as a remarkable change. In agreement with this finding, Campinas and Rosa [45] reported that CFV particularly matters for high membrane fluxes. They investigated the effect of powdered activated carbon (PAC) particles on NF at different CFVs. Even for PAC particles, which are large enough (6 mm average diameter) to avoid membrane pore blocking, there was no advantage in working at higher CFVs. They observed a similar flux decrease pattern for CFVs of 0.5 and 1.0 m/s. They indicated that convective flux had no effect under laminar flow conditions.

As can be seen from Table 8, the flux decline with respect to the clean water flux at steady state was only 2.1% for the lower CFV of 0.7 m/s and 9.8% for the higher CFV of 1.2 m/s. This level of flux decline did not indicate severe fouling, despite a very high rejection of organic matter. Thus, operating the DL-NF at a lower CFV appeared beneficial in terms of removal efficiency and fouling characteristics.

### 3.4. Effect of transmembrane pressure

The effect of TMP was assessed with pre-filtered surface water at the CFV of 1.2 m/s using the DL-NF membrane. The transmembrane pressure was lowered to 3.5 bars

from the earlier tested level of 6.9 bars, and the removals presented in Table 9 were observed. As can be seen, there occurred no change in the sulfate removal with the decrease in TMP. However, the UV absorbance retention appeared to decrease slightly from 80.7% to 78.0%, with a decrease in TMP. Similarly, conductivity retention decreased from 57.4% to 44.8%, with a decrease in TMP. Although there was no considerable effect of TMP on the retention of sulfate, UVA<sub>254</sub> and conductivity, as expected, there was an increase in the permeate flux from 42.6 to 51.6 L/m<sup>2</sup> h with an increase in TMP.

The effect of TMP was also evaluated in terms of flux decline since it directly affects productivity. In Table 10, water flux, flux decline, permeance, and fouling levels are presented for the experimental runs conducted at 3.5 and 6.9 bar TMP using the DL-NF membrane. The raw water flux at 3.5 bar decreased by about 18% (from 51.6 to 42.6 L/m<sup>2</sup> h) with reference to the flux at 6.9 bar. The decrease in the permeate flux with a decrease in TMP

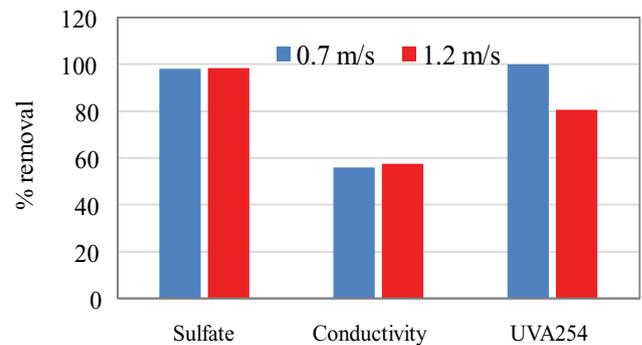


Fig. 3. Steady-state sulfate and conductivity retention with the DL-NF membrane at different CFVs (TMP = 6.9 bar, with MF pretreatment).

Table 8  
Water flux, flux decline and fouling for the DL-NF membrane at different CFV (TMP = 6.9 bar, with MF pretreatment)

CFV (m/s)	Permeate flux (L/m <sup>2</sup> /h)					Flux decline (%)			
	Clean water			Raw water		Total	Due to concentration polarization	Due to fouling	Due to irreversible fouling
	$J_{cwi}$	$J_{cwf}$	$J_{cwc}$	$J_{rw}$	$J_{rw}/J_{cwi}$				
0.7	70.6	69.1	69.5	69.1	0.98	2.1	None	2.1	1.6
1.2	57.2	55.0	56.7	51.6	0.90	9.8	6.2	3.8	0.9

Table 9  
Steady-state sulfate and conductivity retentions with the DL-NF membrane at different TMPs (CFV = 1.2 m/s, with MF pretreatment)

TMP (bar)	Permeate flux ( $J_{rw}$ ) (L/m <sup>2</sup> h)	Permeate sulfate (mg/L)	Sulfate removal (%)	Conductivity retention (%)	Decrease in UVA <sub>254</sub> (%)
3.5	42.6	7.0	98.1	44.8	78.0
6.9	51.6	6.5	98.4	57.4	80.7

Table 10  
Water flux, flux decline and fouling for the DL-NF membrane at different TMPs (CFV = 1.2 m/s, with MF pretreatment)

TMP (bar)	Permeate flux (L/m <sup>2</sup> h)				Raw water permeance (L/m <sup>2</sup> h bar)	Raw water permeance (L/m <sup>2</sup> h bar)	Flux decline (%)			Fouling resistance (m <sup>-1</sup> )				
	Clean water		Raw water				Concentration polarization	Fouling	Irreversible fouling					
	Initial	Final	Initial	Final										
6.9	$J_{cwf}$	57.2	55.0	$J_{rw}$	51.6	$P_{cwf}$	7.5	$(J_{cwf}-J_{rw})/J_{cwf}$	9.8	$(J_{cwf}-J_{fwi})/J_{cwf}$	3.8	$(J_{cwf}-J_{fwi})/J_{cwf}$	0.9	4.98E+14
3.5		45.6	45.9		42.6	$P_{cwf}$	10.7 ± 3.4		6.6		None		0.7	4.72E+14

is an expected phenomenon, as reported by Tu et al. [46] and Alventosa-deLara et al. [47]. Nevertheless, raw water permeance values which provide a better insight into flux behavior indicated that the permeances of the DL-NF membrane at the 3.5 and 6.9 bar TMP are similar. Besides, there is no statistically significant difference between the raw water (12.2 and 7.5 L/m<sup>2</sup> h bar) and pure water permeances (10.7 ± 3.4 L/m<sup>2</sup> h bar) (Table 10). This finding was further confirmed by the fouling resistances calculated. When the flow resistances caused by fouling were compared with each other, it was seen that there is almost no difference between the fouling resistances, and TMP did not affect the flow resistance in raw water filtration. On the contrary, Satyanarayana [48] and Varol et al. [49] reported that the particle deposition on the membrane surface that comes into existence faster at higher TMPs could reduce flux by forming a second boundary layer as a result of concentration polarization. However, these researchers worked with wastewaters rather than water, and therefore the membrane fouling due to concentration polarization was remarkable.

#### 4. Conclusion

This study was focused on testing the efficiency of three commercially available NF membranes (DK-NF, NF270, and DL-NF) for sulfate separation from high sulfate-containing drinking water. The following conclusions were drawn:

- The NF270 and DL-NF membranes provided over 98% rejection of sulfate. However, the DK-NF membrane was able to provide 82% rejection.
- An excellent flux recovery was achieved via membrane chemical cleaning for both NF270 and DL-NF membranes.
- Based on the overall results, the NF270 membrane appeared to be the best among the three membranes tested.
- When the effects of CFV on NF performance using the DL-NF membrane were investigated, it appeared that the permeate flux and sulfate rejection did not change significantly with an increase in CFV.
- It was very promising that the drop from 6.9 to 3.5 bar in TMP did not lead to a decrease in sulfate rejection. Besides, there was no change in fouling resistance with a reduction in TMP. This finding indicated that energy costs would be significantly reduced when NF is applied on a real scale using the DL-NF membrane.

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