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Simultaneous removal of Cr(VI) from water containing sulfate using nanofiltration

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ABSTRACT

In this paper, various parameters such as pressure, pH, and concentration levels were investigated. The Cr(VI) and sulfate concentrations chosen for the study were the same as the levels found in drinking water sources. The results indicated that a better rejection of Cr(VI) (96%) was obtained at basic pH and at an optimal pressure of 4 bar in 0.1 mg/L and no significant effect was found between 4 and 8 bar in 0.5 mg/L concentrations. Permeate fluxes were 12.8 and 10.53 L/m^2 h at 4 bar in 0.1 and 0.5 mg/L concentrations, respectively. In the presence of a fixed sulfate concentration, fluxes declined with the increasing ionic strength of Cr(VI) feed solutions. The simultaneous rejection of sulfate and Cr(VI) (varying from 90% to 100%) showed that the influences of the ionic strength of a mixed aqueous solution were found to be weak at the selected concentrations of both Cr(VI) and sulfate. The experiments also showed that the rejection was affected more by the ion strength of Cr(III) than by Cr(VI). To demonstrate the fate of the ions rejected, a mass balance analysis was developed under optimal experimental conditions.

Keywords: Nanofiltration; Hexavalent chromium; Sulfate; Rejection; Permeate flux

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1. Introduction

Some groundwater sources used for drinking purposes contain an increased concentration of ions, such as hexavalent chromium, as well as some other dissolved components, such as sulfate, at the upper value of the established maximum concentration levels (MCL$_s$). Cr(VI) is an oxyanion known to cause various health problems, such as allergic reactions, skin rashes, lung cancer, and kidney and liver damage [1]. A risk-based drinking water standard of 50 µg/L has been established for Cr(VI) [1] according to WHO standards. For sulfate, although its health effects are relatively short-term, it is clear that water with a sulfate level exceeding 400 mg/L should not be used in the preparation of infant formula [2]. Older children and adults can experience diarrhea and dehydration from exposure to sulfate. To prevent negative health

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effects, chromium and sulfate, which are often are simultaneously present in groundwater, must be removed from drinking water before distribution to consumers. In the literature, conventional treatment methods proposed for chromium are adsorption, chemical precipitation, ion exchange, and membrane technology processes [3,4]. Among these methods, ion exchange and membrane technology are also typically capable of removing sulfate from drinking water. Due to the developments of membrane production technology, extensive attention has been paid in recent years to the application of membrane technology for water treatment [5,6]. The simultaneous removal of Cr(VI) and sulfate by using nanofiltration (NF) as a membrane method is more cost-effective than a combination of two conventional techniques, such as chemical precipitation and ion exchange or activated carbon [7]. The quality of NF can be changed by using different membrane types, and a greater amount of water fluxes can be achieved at lower pressures than for reverse osmosis (RO) membranes [8]. Therefore, due to its relatively low energy costs [9,10], the development of new applications, and in view of health, environmental, and economic concerns, NF has recently attracted increasing attention for the removal of heavy metals and divalent dissolved salts from water [5]. NF membranes are usually negatively charged [2] with a selective thin layer coating supporting the porous membrane layer that controls all the transport properties by diffusion, convection, and Donnan exclusion mechanisms [5]. The charged nature of the membrane surface allows for the selective separation of heavy metals as well as inorganic solutes at a relatively lower pressure of operation than that of RO [7]. Many researchers have investigated the influence of physicochemical behavior [4] and pH [5] on NF. Their studies showed that rejection depends on the ionic strength and pH (up to 80% at a pH of 8) of water [6]. Most of the studies on chromium removal have been for 5–2,000 mg/L concentrations [4,5], which are above the level found in drinking water sources. Thus, there is a lack of information on chromium removal by NF for drinking water levels (<0.1–0.5) mg/L. To the best of our knowledge from available literature on NF, no reports could be found either on Cr(VI) removal at low levels, or on simultaneous removal of Cr(VI) and sulfate from contaminated drinking water. Therefore, the main purpose of the present study is to evaluate the behavior of NF for the simultaneous removal of Cr (VI) and sulfate from water. To achieve this, the effects of the most important contributing factors, i.e. pressure, pH, permeate flux, and concentration, were evaluated for the removal of the above-mentioned contaminants using NF.

2. Materials and methods

2.1. Experimental setup and procedure

All of the experiments were carried out in a pilot-scale membrane unit made of stainless steel and equipped with one polyamide spiral-wound membrane type NF90 (Film Tec Corporation). Fig. 1 shows the schematic diagram of the pilot-scale experimental setup used in this study.

For more uniform inlet concentration of target species, the unit was operated in batch once through mode, which means that permeate and concentrate were not mixed. The membrane unit was operated as cross-flow into which the feed solution was injected by a high pressure pump (Lowara, Italy) equipped with a pressure-regulating valve manually adjusted to maintain constant pressure. The characteristics of the studied membrane are shown in Table 1.

The volume of the feed solution was 20 L, excluding the amount in the tubes of the installation. The trans-membrane pressure (TMP) selected to study NF ranges between 2 and 10 bar. The minimum pressure was selected to be as cost-effective as possible. Preliminary experiments indicated that the pure water flux did not change significantly after 45 min; therefore, samples of permeate were collected after 45 min of filtration. The parameters taken into account for measuring the NF performance were the observed retention (R), pure water flux, and permeate flux calculated from the following Eqs. (1)–(3), respectively:

Rejection (retention)

$$R\% = (1 - C_p/C_o) \times 100 \tag{1}$$

pure water flux

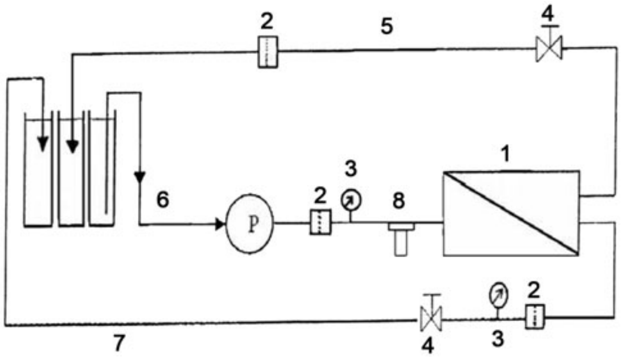

Fig. 1. Schematic of the experimental setup. (1) pressure vessel with NF membrane, (2) flow meter, (3) pressure sensor, (4) pressure regulating valves, (5) permeate line, (6) feed solution, (7) retentate line, and (8) cartridges filter.

Table 1
Main characteristics of the studied membrane

Parameter	NF90-4040
Type	Polyamide TFC
Configuration	Spiral wound
Membrane area, m^2	7.6
Length, mm	1,016
Diameter, mm	99
Permeate flow rate, m^3/d	7.6
Max operating temperature, ℃	45
pH range, continuous operation	2–11

$$J_{\mathrm{VP}} = V_{\mathrm{pw}}/A \cdot t \tag{2}$$

permeate flux

$$J_{\mathrm{V}} = V_{\mathrm{P}}/A \cdot t \tag{3}$$

where C_p and C_o are the concentration in the permeate and in the feed solutions, respectively; J_{vp}, L/h m^2; J_v, L/h m^2; V_{pw} = volume of pure water permeate collected per unit time t, L/h; V_p = volume of permeate collected per unit time t, L/h; and A = area of the membrane, m^2. After each test, the membrane was rinsed using 1% citric acid for 5 min (mixed with sodium hydroxide to obtain a pH 4) and then pure water (10 min) to remove the scale [11]. To demonstrate the fate of the rejected ions by membrane, a mass balance analysis was developed for the unit boundary under optimal experimental conditions. The instrument was operated at a room temperature of 25 ± 2℃.

2.2. Analytical methods

The basic compounds used in the study were solutions of Na_2SO_4, $Cr_2O_7K_2$, NaCl, and anhydrous $CrCl_3$, $6H_2O$, all prepared with demineralized water. All salts were purchased from the Merck Corporation and were over 99.9% pure. The concentration of Cr(VI) was analyzed using a UV–vis spectrophotometer (Unico UV-2100) at 540 nm wave length by using 1, 5-diphenylcarbazide as a color complexion agent based on the procedure detailed in the standard methods [12]. Cr^{3+} was measured using flameless atomic absorption (Shimatzu model AA 670 G) at 357 nm. Sulfate was analyzed using the Turbidimetric Method 4500-SO_4^{2-} E) [12]. All of the prepared calibration curves were linear over a concentration range 0–0.5 mg/L (for Cr) and 0–400 mg/L (for sulfate) with R^2 greater than 0.99. The adjustment of pH was made using 1 N NaOH and HCl with a pH meter (JENWAY 3505). To ensure the repeatability of the data, all experiments were conducted in duplicate and the average of the results was reported.

3. Results and discussion

The behavior of hexavalent and trivalent chromium separation in the NF process under different operating conditions including pressure, feed concentration and pH (Table 2) is presented and discussed in the following section.

3.1. Effect of type of chromium species on nanofilter performance

Because one of the major factors influencing the retention of salts by a membrane is the distribution of charged ions between the membrane and solutions, the concentration of co-ions (ions with the same charge as the membrane) and counter-ions (ions with an opposite charge to the membrane) can affect the rejection of compounds in solution and thus the overall NF performance. A potential difference between solution and membrane, known as the Donnan potential [3,6,13], can maintain the electrochemical equilibrium. The co-ions are repulsed by the membrane while the counter-ions are attracted. As shown in Fig. 2, the effect of chromium species on rejection in the NF system was investigated at different TMP_s ranging from 2 to 10 bar.

Table 2
Experimental phases and conditions

Phase	Cr(VI) (mg/L)	Cr(III) (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	P (bar)	pH	MBA
1	0.1–0.5	–	–	–	2–10	–	–
2	0.1,0.5	0.1, 0.5	100–800	–	2–10	4–9	–
3	0.1,0.5	0.1, 0.5	400	400	4, 8	7	–
4	0.1	–	400	400	2–10	7	*

Notes: MBA = mass balance analysis; *mass balance analysis were performed in phase 4.

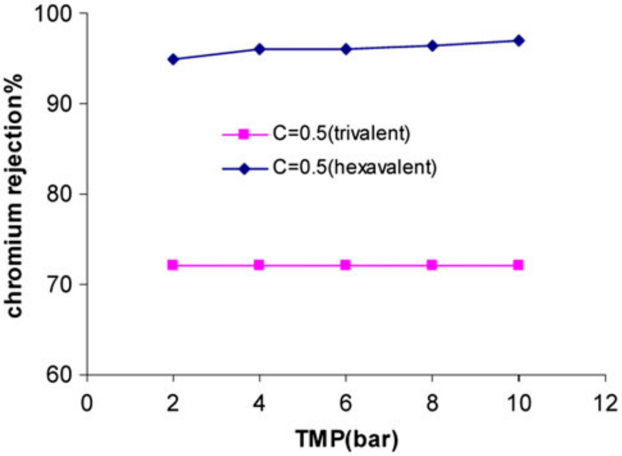

Fig. 2. Rejection vs. pressure for various concentrations of tri- and hexavalent chromium (temperature: 25˚C and neutral pH (7.2–7.4)).

Because of the attraction of positively charged Cr(III), rejection was not affected by increased pressure and was lower than hexavalent chromium at the same pressure [4], meaning that a negatively charged surface membrane would influence the best retention of chromate. Therefore, for all TMP_s, the rejection percent of Cr^{6+} was on average 22% higher than Cr^{3+} rejections. In addition, Fig. 2 shows that there is no significant effect between TMP 4 and TMP 8 in 0.5 mg/L concentration. Fig. 3 presents the trend of permeate flux vs. TMP_s for Cr^{3+} and Cr^{6+}.

As seen in Fig. 3, the permeate flux increased with the increase of TMP for both chromium species. This is because the permeate flux increases with the increase of TMP by the transport phenomenon of NF membranes. This result can be explained by irreversible thermodynamics and the relationships that have been proposed by Kedem and Katchalsky [3].

Additionally, the curves in Fig. 3 show that the permeate flux of the trivalent and hexavalent chromium ions has similar trends of increasing pressure, but the differences in the flux of the two species of chromium increased as pressure increased. For example, at a pressure of 10 bar, the flux percentage of Cr(VI) was on average 44% higher than Cr(III) flux. This result could be due to the polarization concentration of counter-ions (Cr^{3+}) on the surface of the nanofilter that decreased the permeate flux. In addition, the linearity of the Cr(III) curve showed that water permeability had a fixed rate by increased TMP.

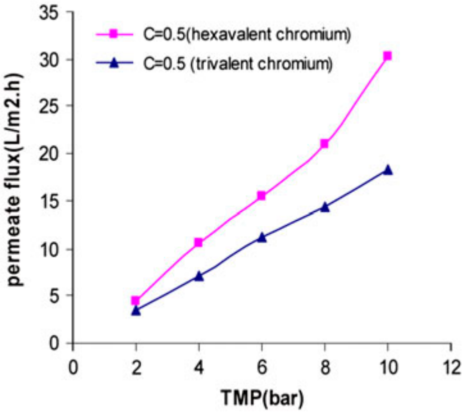

Fig. 3. Permeate flux as a function of TMP for various species of chromium (temperature: 25˚C and neutral pH (7.2–7.4)).

3.2. Effect of pH on chromium

Speciation studies of Cr(VI) in aqueous solution, on the basis of spectrophotometry, electrochemistry, indicate the existence of the following equilibria;

$$H_2CrO_4 = H^+ + HCrO_4^- \tag{4}$$

$$HCrO_4^- = H^+ + CrO_4^{2-} \tag{5}$$

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \tag{6}$$

Equilibria are dependent on pH, with $HCrO_4^-$ and $Cr_2O_7^{2-}$ existing primarily in acidic media and CrO_4^{2-} being the lone species of Cr(VI) above pH 7.0. At higher pH range, the fraction of $Cr_2O_7^{2-}$ species rapidly decreases with increasing pH above 5. In the removal of Cr(VI) process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species will be represented as Cr(VI). In the neutral solution at low

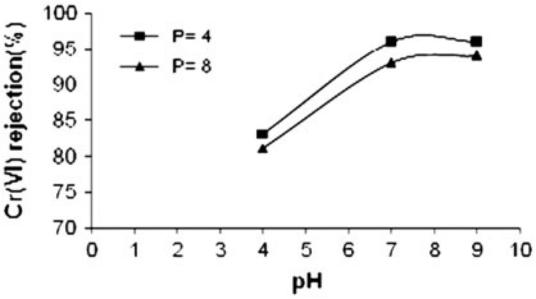

Fig. 4. Cr(VI) rejection vs. pH at TMP_s (temperature: 25˚C and C = 0.1 mg/L).

concentrations, Cr(VI) will be present in the form of $HCrO_4^-$ and CrO_4^{2-}. At acidic pH, $HCrO_4^-$ is the predominant Cr(VI) species in the aqueous phase. Fig. 4 represents the rejection of Cr(VI) from water as a function of pH at TMP_s = 4 and 8 bar. Fig. 4 shows that the rejection of Cr(VI) increased with the increase of pH at all pressures.

It is clear that as pH is increased, bivalent ions of chromium ($CrO_4^{2-}/Cr_2O_7^{2-}$) were formed; this confirmed the higher rejection in alkaline range with high efficiency [5]. This particular phenomenon may be explained by the fact that the hexavalent chromium is present in different ionic forms at different pH conditions. Basically, the hexavalent chromium normally remains in the form of chromic acid (H_2CrO_4) at very acidic pH condition and it changes to acid chromates ($HCrO_4$) of different concentrations with respect to pH up to 6.5. Further at higher pH values beyond 7, it gets transformed to chromates (CrO_4^{2-}) of different concentrations. The dichromate ($Cr_2O_7^{2-}$) ion concentration is also present and it depends on the feed concentration with respect to pH. Dichromate concentration is reduced by further increasing the pH. The change in rejection with the variation of pH value is quite expected due to the changes in the relative amount of monovalent, di-, and multivalent ions present in the system. As seen in Figs. 4 and 5, the presence of different ions of hexavalent chromium as explained earlier and its dependence on pH condition as well as feed concentration (low chromium concentration) is thus the main factor influencing the specific chromium rejection behavior at the prevailing condition. Therefore, in basic pH condition, where the dissociation is relatively high for low chromium concentration, rejection of divalent ions is high at pH > 7 and is stable at pH 9 for both TMP = 4 and 8 [4]. Due to higher and lower rejection at 4 and 8 bar respectively, these two pressures were chosen for investigation with different salt mixtures and fixed Cr(VI) concentrations. As seen in Fig. 4, rejection of Cr(VI) at each pH increased with the decrease of pressure. For example, at pH 7, the rejection percentage of Cr^{6+} at 4 bar was on average 7% higher than that of 8 bar. This finding could be due to the small ionic radius size of Cr^{6+} (0.14 nm) [13], which could pass through the filter with increasing pressure.

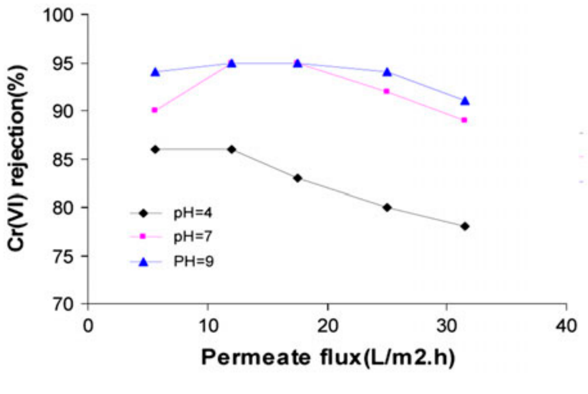

Fig. 5. Cr(VI) rejection vs. permeate flux as a function of pH (temperature: 25˚C and C = 0.1 mg/L).

Fig. 5 shows the rejection vs. permeate flux as a function of pH. It also shows that the best rejection in neutral (7.2–7.4) and basic pH is related to permeate flux = 12–18 L/m^2h, which was done at p = 4–6 bar (as indicated in Fig. 4).

3.3. *Removal of Cr(VI) in the presence of sulfate and vice versa*

Geological situation and/or anthropogenic contamination through the discharge of industrial effluents cause an increased concentration of ions such as hexavalent chromium as well as some other dissolved components such as sulfate at the upper values of the established MCL_s in water sources. Therefore, the performance of NF for removal of Cr(VI) in the presence of various concentration of SO_4^{2-} was investigated under the conditions presented in Table 2. Fig. 6 shows that an increase of sulfate leads to a decrease of the retention of hexavalent chromium at 4 and 8 bar. This finding could not only be explained by the anion size (the ionic radius of sulfate = 0.23 nm [13] is larger than chromium = 0.14 nm) but also by the effect of its charge, i.e. Cr(VI) rejection is reduced due to the reduced effect of electric double layer (upwards of 600 mg/L) as a result of increased concentration of sulfate when some concentration accumulation occurs. Therefore, the observed retention sequence for the membrane examined is $SO_4^{2-} > CrO_4^{2-}$.

The effect of various feed concentration on the rejection for solute Na_2SO_4 in the presence of Cr(VI)

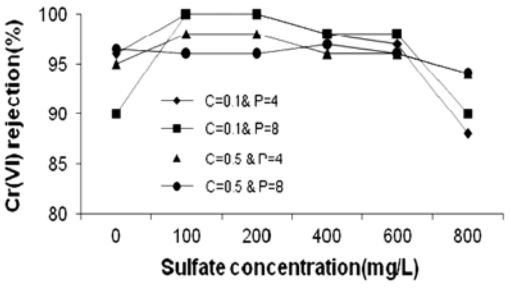

Fig. 6. Cr(VI) rejection in NF as a function of sulfate concentration at moderate and high TMP.

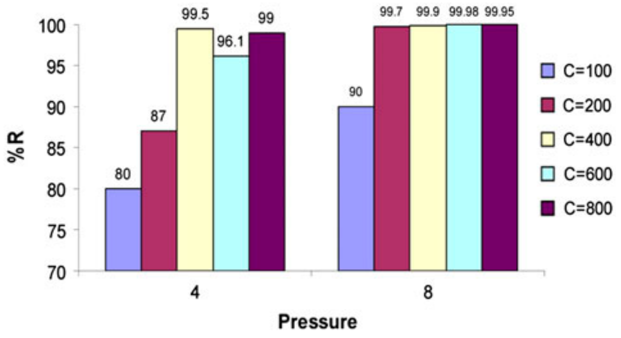

Fig. 7. Various concentrations of sulfate removal vs. TMP (bar) in Cr(VI) = 0.5 mg/L.

concentration of 0.5 mg/L is shown in Fig. 7. Because of Donnan exclusion (repulsion of co-ions) and the lower diffusion coefficient of sulfate ($1.06^{*}10^{-9}$ m^2 s^{-1}) [14], sulfate rejection was very high in binary solution.

Table 3 shows that 95.59 and 79.56% of accumulated sulfate in feed solution on a nanofilter at 8 and 4 bar, respectively. Therefore, an increase of sulfate concentration leads to the increase of sulfate rejection by polarization concentration of sulfate on the nanofilter's surface and the higher rejection of sulfate [15].

In the case of sodium salts of sulfate and chloride as the smallest ion, a mixed aqueous solution of NaCl, Na_2SO_4, and Cr(VI) increased chromium retention at each pressure level (Fig. 8). According to Fig. 8, chromium rejection varied from 98 to 100% at 4 bar and 98.3 to 99.6% at 8 bar.

The solute NaCl was able to freely transport through the NF, while 98% of the solute Na_2SO_4 was rejected. Therefore, the high rejection of sulfate led to a higher rejection rate of Cr(VI). These results can be interpreted in terms of the Donnan exclusion. In comparison with individual rejection of Cr(VI) at the same concentration and pressure, the influence of the ionic strength of mixed aqueous solution for Cr(VI) removal was found to be weak.

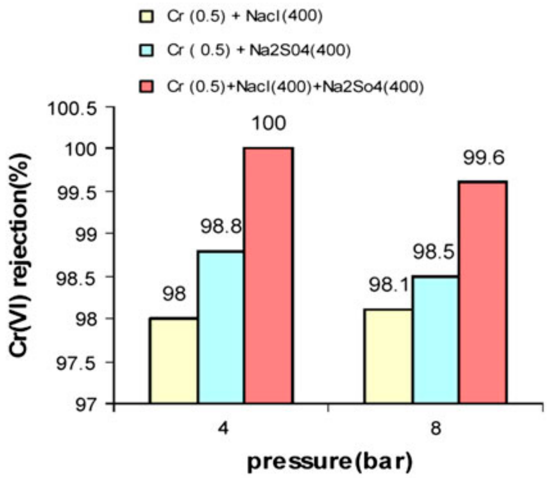

Fig. 8. Cr(VI) rejection as a function of pressure in various binary and mixed aqueous solutions.

To demonstrate the fate of the rejected ions by membrane, a mass balance analysis (Table 3) was developed under the best experimental conditions (Table 2). The difference between the feed concentrations of each parameter and the total sum of permeates and concentrates creates the mass of components to get accumulated on the nanofilter. Table 3 shows that pressure of 4 bar (100% removal of Cr^{6+}) is most likely suitable from the perspective of human health. However, a pressure of 10 bar could discharge 81.8 and 97.32% of concentrated Cr^{6+} and sulfate, respectively, in the concentrate discharge line. In addition, the presence of 3.65 and 2.67% of Cr(VI) and sulfate, respectively, on the nanofilter could decrease the frequency of cleanings, prevent scaling, and lower the required pressure, which makes it both environmentally friendly and cost effective.

Table 3
Mass balance analysis

							Mass balance analysis								
	Feed concentration (mg/L)			Permeate rejection (%)			In permeate (%)			In concentrate (%)			On nanofilter (%)		
P (bar)	Cr (VI)	Sulfate	TDS	Cr	Sulfate	TDS	Cr	Sulfate	TDS	Cr	Sulfate	TDS	Cr	Sulfate	TDS
2	0.1	500	2,500	85	100	99.7	15.45	0	0.23	36.36	65.9	33.6	48.18	34.08	66.15
4	0.1	500	2,500	100	99.6	99.7	0	0.43	0.24	0	20	21.9	100	79.56	77.85
6	0.1	500	2,500	100	100	99.8	0	0	0.29	0	2.96	7.03	100	97.03	92.66
8	0.1	500	2,500	92	99.7	99.8	8.33	0.37	0.2	12.5	4.04	5.72	79.17	95.59	94.07
10	0.1	500	2,500	86	100	99.7	14.54	0	0.28	81.8	97.32	84.63	3.65	2.67	15.07

4. Conclusions

In this study, we presented and explained the performance of an NF membrane for the simultaneous removal of chromium, a toxic inorganic, and sulfate ions from water. From the mixed binary salt phase of the study, we showed that Cr(VI) rejection decreased in the presence of sulfate at sulfate concentrations greater than 400 mg/L (i.e. 600 mg/L), but not in the presence of mixed aqueous solutions of NaCl and Na_2SO_4 at concentrations selected for our study. In addition, the results indicated that the type of chromium species in feed solutions, driven pressure and pH had significant effects on NF; but, the influence of salt addition and ionic strength was found to be insignificant. Data revealed that NF technology was efficient and thus applicable for the simultaneous removal of Cr(VI) and sulfate from water.

Acknowledgments

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