

Removal of hexavalent chromium from brackish groundwater by nanofiltration: a case study in Iran

B. Barikbin, S. B. Mortazavi and G. Moussavi

ABSTRACT

The hexavalent chromium Cr (VI) and sulfate concentrations in some groundwater sources used for drinking water in Birjand, the capital of Southern Khorasan Province, Iran, are greater than the established maximum concentration levels (MCLs). In this work, a nanofiltration system was examined as a promising method for the simultaneous removal of Cr (VI) and sulfate from groundwater. The effects of operating pressures (2–10 bar) on Cr (VI) (0.1–0.5 mg/l) for and sulfate (800 mg/l) were investigated. Experimental results in Birjand drinking water indicated that a better rejection of Cr (VI) (96%) was obtained at basic pH and at an optimal pressure of 4 bar. In addition, an increase of sulfate (up to 600 mg/l) led to a decrease in the retention of hexavalent chromium at 4 and 8 bar, respectively. We did mass balance analysis to show the fate of the rejected ions by membrane. On the basis of our results, NF90 had much more efficient removal ($R > 94\%$) for all monovalent and divalent anions and cations and appeared to be applicable for the removal of Cr (VI) and sulfate from the Birjand drinking water.

Key words | brackish water, hexavalent chromium, nanofiltration, rejection, sulfate

B. Barikbin

S. B. Mortazavi (corresponding author)

G. Moussavi

Department of Environmental Health,

Faculty of Medical Sciences,

Tarbiat Modares University,

Tehran,

Iran

E-mail: mortazav@modares.ac.ir

INTRODUCTION

Due to the local geological formations, some groundwater sources used for drinking purposes in Birjand, capital of Southern Khorasan Province, Iran, contain concentration of hexavalent chromium Cr (VI), and total dissolved solids (TDS; any minerals, salts, metals, cations or anions dissolved in water) at values greater than the established maximum concentration levels (MCLs) (0.05 and 500 mg/l, respectively) (WHO 2008). Cr (VI) is known to cause various adverse health effects such as allergic reactions, skin rashes, lung cancer, and kidney and liver damage (WHO 2008). The conventional methods used to remove chromium are adsorption, chemical precipitation, ion exchange and membrane processes (Hafiane *et al.* 2000).

Furthermore, TDS at high concentrations (exceeding 500 mg/l) can give water a bitter or salty taste, result in encrustations, films or precipitates on fixtures, the corrosion of fixtures, and can reduce the efficiency of water filters (Wilkes University 2007). TDS is used as an indicator to determine the general quality of the water. The results of analysis of Birjand groundwater showed that sulfate is the major anion in water.

Elevated levels of sulfate can cause diarrhoea and dehydration in consumers. Infants are often more sensitive to sulfate than adults. Therefore, water with a sulfate level higher than 400 mg/l should not be used in the preparation of infant formula (WHO 2008). Distillation, ion exchange and membrane technology are three types of treatment systems capable of removing sulfate from drinking water (Haghsheno *et al.* 2009).

Therefore, to prevent harm caused by chromium and sulfate which often are simultaneously present in the Birjand brackish groundwater, these compounds must be removed from drinking water before it is distributed. In view of health, environmental and economic concerns, nanofiltration (NF) has attracted increasing attention over recent years for the removal of heavy metals and divalent dissolved salts from water (Boussu *et al.* 2008). Membranes for NF are generally characterized by a high charge density and pore sizes in the range of nanometers. The surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes (Bartels *et al.* 2008). The rejection characteristics of NF

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membranes depend on chemistry and surface charges of the separating barrier layer, ionic composition and concentration of feed water, and operating parameters of the NF system; these are the recovery rate and permeate flux (Bartels *et al.* 2008). Several researchers have performed fundamental studies to understand the mechanisms behind multivalent ion removal in NF and have showed the separation of charged solutes is based on both ion size and Donnan exclusion (Ouyang *et al.* 2008). In this study, we tried to better understand the phenomena responsible for retention of monovalent and divalent anions such as Cl, Cr (VI) and sulfate. To identify the ionic interactions between divalent anions and monovalent ions, we successively studied mixtures of Na₂SO₄, NaCl, and Cr₂O₇K₂ of increasing complexity. Many researchers have used NF to remove chromium or sulfate individually from water (Hafiane *et al.* 2000; Taleb-Ahmed *et al.* 2002; Muthukrishnan & Guha 2008; Yoon *et al.* 2009). They investigated the influence of physicochemical behavior, ionic strength, and pH of Cr (VI) solution on NF. Their studies on Cr (VI) showed that rejection depends on ionic strength and pH (up to 80% at pH 8) of water (Hilal *et al.* 2004). Most of the research reported Cr (VI) removal in high concentrations (5–2000 mg/l) (Hafiane *et al.* 2000; Taleb-Ahmed *et al.* 2002), which is beyond the level found in Birjand drinking water (<0.1 mg/l). Therefore, the goal of this work was to study the simultaneous removal of Cr (VI) and SO₄²⁻ from Birjand drinking water.

MATERIALS AND METHODS

Experimental set-up and procedure

To acquire the experimental data necessary for the Birjand water treatment plant design, synthetic water, which was

prepared similarly to natural water, was passed through nanofiltration at the beginning of the study. The preceding experiments were undertaken to examine commercial nanofiltration membrane performance with single, binary and mixed aqueous solution salts in synthetic water. To perform this, the effects of the most important operational parameters, i.e., pressure, pH, permeate flux, and concentration were evaluated for the removal of target contaminants using NF. The nanofiltration process under different phases and operation conditions including pressure, feed concentration, and pH are presented in Table 1. On the basis of operational results reported from the first four phases, the final phase (phase 5) and mass balance analysis was done for Birjand (natural) drinking water (Table 1).

All of the experiments were carried out in a pilot-scale membrane unit made of stainless steel equipped with a unit of polyamide spiral-wound membrane type NF90 (Film Tec Corporation), which has the following characteristics: length 1016 mm, membrane area 7.6 m², diameter 99 mm, stabilized salt rejection (%) >97.0 and molecular weight cut-off 200 Da (Figure 1). To ensure a uniform inlet concentration of target species, the unit was operated in batch once through mode, which means 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) and was controlled by a frequency converter manually adjusted to maintain a constant feed and pressure. The trans-membrane pressure (TMP) was selected to investigate NF ranges between 2 and 10 bar. Samples of permeate were collected after 15 minutes of filtration. The parameters take into account when measuring the NF performance were the observed retention (*R*), pure water flux and permeate flux calculated from Equations (1)–(3), respectively:

Table 1 | Experimental phases and conditions

Phase	Type of water	Cr(VI), mg/l	SO ₄ ²⁻ , mg/l	Cl ⁻ , mg/l	Pressure (bar)	pH	Mass balance analysis
1	Synthetic	0.1–0.5	-	-	2–10	-	-
2	Synthetic	0.1, 0.5	100–800	-	2–10	4–9	-
3	Synthetic	0.1, 0.5	400	400	4, 8	7	-
4	Synthetic	0.1	400	400	2–10	7	-
5	Birjand	0.1	390	240	4	8.2	*

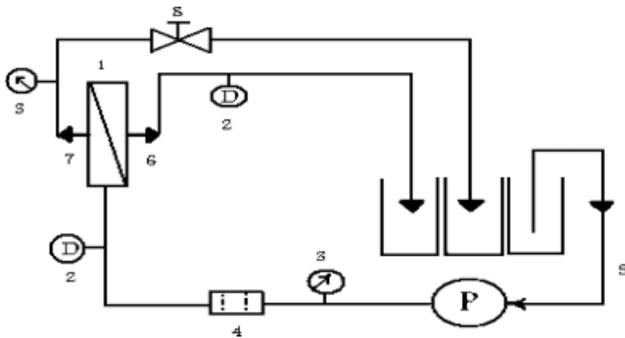


Figure 1 | Schematic of the experimental set up: (1) NF membrane; (2) flowmeter; (3) pressure sensor; (4) frequency converter; (5) feed solution; (6) permeate flow; (7) retentate flow; (8) pressure regulating valve.

Rejection (retention)

$$R\% = (1 - C_p/C_o) \times 100 \quad (1)$$

Pure water flux

$$J_{VP} = V_{pw}/A.t \quad (2)$$

Permeate flux

$$J_V = V_p/A.t \quad (3)$$

where C_p and C_o are the concentrations in the permeate and in the feed solutions, respectively; J_{vp} , L/h.m²; J_v , L/h.m²; 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, m².

After each test, the membrane was rinsed using 1% (W) sodium hydroxide for 5 min and then pure water (10 min) to remove the scale. The instrument was operated at a room temperature of $25 \pm 2^\circ\text{C}$. Finally, to show the fate of the rejected ions by membrane, a mass balance analysis was developed under optimal experimental conditions (Table 1). Differences between feed concentrations of each parameter with a sum total of permeate and concentrate gave the mass of the component that accumulated on the nanofilter.

Analytical methods

At the beginning of study, Birjand drinking water was analyzed; the compositions of the natural and synthetic water are given in Table 2. The basic compounds used to study were

solutions of Na_2SO_4 , NaCl and $\text{Cr}_2\text{O}_7\text{K}_2$, which were prepared by dissolving given amounts of salts in distilled water. All salts were purchased from Merck Corporation with purity over 99%. Concentration of Cr (VI) was analyzed using a UV-Vis spectrophotometer (Unico UV-2100) at 540 nm wavelength by using 1, 5-diphenylcarbazide as a color complexing agent based on the procedure detailed in the standard methods (APHA et al. 2005). Sulfate concentration was analyzed by the turbidimetric method 4500-SO₄²⁻ E (APHA et al. 2005).

All the prepared calibration curves were linear over a concentration range of 0–0.5 mg/l for Cr (VI) and 0–400 mg/l for sulfate and chloride with R^2 greater than 0.99. Alkalinity was determined by titration to a fixed pH while electrical conductivity was measured by a conductometer (Orion model 124). The adjustment of pH was made using 1 N NaOH and HCl and a pH meter (Jenway 3505). To ensure the repeatability of data, all samples were prepared and tested at least in duplicate and the averages of results were reported.

RESULTS AND DISCUSSION

Removal of Cr (VI) in synthetic water

In Figures 2 and 3, the performance of NF for removal of Cr (VI) in phase 1 and 2 is presented (Table 1). Figure 2 shows that the decrease of Cr (VI) concentration leads to fluctuating retention of chromium at 4 and 8 bar. At the lower

Table 2 | Composition of the natural (Birjand) and synthetic water

Parameter	Birjand	Synthetic
Sulfate (mg/l)	390	400
Cr(VI) (mg/l)	0.1	0.1, 0.5
DOC (mg/l)	NA	-
Alkalinity (mg/l, as CaCO ₃)	200	220
Total hardness (mg/l, as CaCO ₃)	415	440
Ca hardness (mg/l, as CaCO ₃)	100	80
Mg hardness (mg/l, as CaCO ₃)	314.5	360
Na ⁺ (mg/l)	230	230
pH	8.2	8.1
Chloride (mg/l)	240	250
TDS (mg/l)	1120	1500
Conductivity (μS/cm)	1611	2000

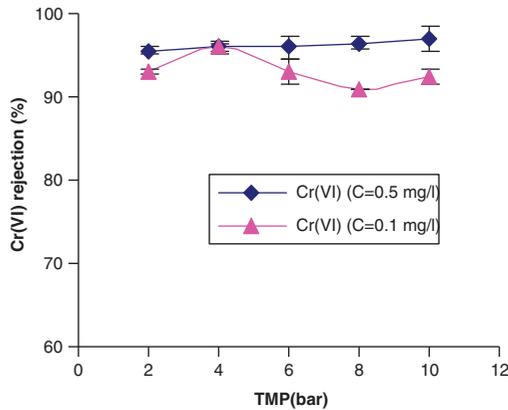


Figure 2 | Cr (VI) rejection as a function of TMP in high and low selected Cr (VI) concentrations at natural pH.

concentration, Cr (VI) rejection decreases with increasing pressure. This finding can be explained by passing the small size of Cr^{+6} (0.14 nm) (Yoon *et al.* 2009) across the filter with porosity factor (ϵ_r) = 0.28 nm (Krieg *et al.* 2004) by increasing pressure. At the higher concentration of Cr (VI), concentration polarization can hinder back diffusion of Cr (VI), and therefore, Cr rejection was increased.

In Figure 3, Cr (VI) rejection versus pH at TMP_s varying from 2 to 10 bar is shown: the rejection of Cr (VI) increased with the increase of pH for all pressures. Due to the higher and lower rejection at 4 and 8 bar, respectively, these two pressures were chosen for investigation with different salts mixtures at fixed Cr (VI) concentrations (Figures 2 and 3). As seen in Figure 3, the rejection of Cr (VI) for each pH increased with a decrease in pressure. For example, at pH=7, the rejection percentage of Cr^{+6} at 4 bar was on average 7% higher than at 8 bar.

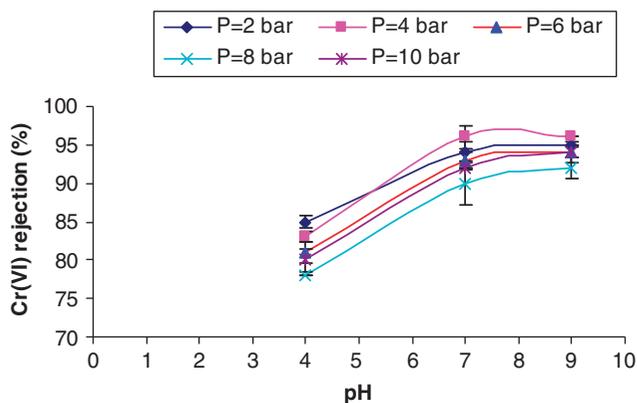


Figure 3 | Cr (VI) rejection versus pH at TMP_s (temperature: 25°C and C=0.1 mg/l).

Figure 4 shows Cr (VI) rejection as a function of TMPs in acidic and basic pH. As shown in Figure 3, the best retention was observed for natural to basic pH levels. Figures 3 and 4 show that as the pH is increased, bivalent ions of chromium ($\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$) are formed, thereby confirming the greater rejection in alkaline ranges with high efficiency (Muthukrishnan & Guha 2008). In addition, increasing pH can increase the negative charge of the membrane surface. Therefore, we expect that the rejection of Cr (VI) will increase with increasing pH. Therefore the Cr (VI) concentration has little influence on rejection in the range of 0.1–0.5 mg/l for each pH (Figure 4).

Simultaneous removal of Cr (VI) and sulfate

As seen in Table 2, there is a high concentration of Cr (VI) and sulfate in Birjand water samples. Therefore, the performance of NF for the simultaneous removal of Cr (VI) and SO_4^{2-} was investigated under the conditions presented in Table 1. Cr (VI) rejection as a function of TMP with various concentrations of sulfate was studied, and the results are shown in Figure 5. Figure 5 shows that an increase of sulfate leads to a decreasing retention of Cr (VI) in TMPs of 4 and 8 bar. Visually, the first point (water without sulfate ion) is lower than the following ones. Therefore, one might assume that there is not a decreasing trend. As can be seen, the first point is related to water containing Cr (VI) without sulfate ions.

The decreasing retention of Cr (VI) (especially for 0.1 mg/l) in the presence of increasing sulfate at 4 and 8 bar (Figure 5) can be explained by considering the effect of their charge and the anion size, i.e., the ionic radius of

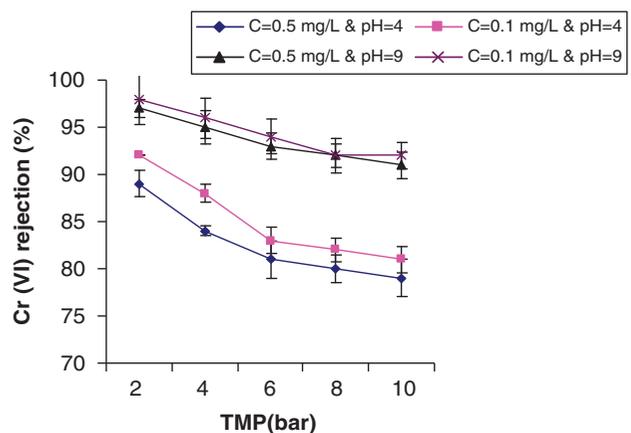


Figure 4 | Cr (VI) rejection as a function of TMP in basic and acidic pH.

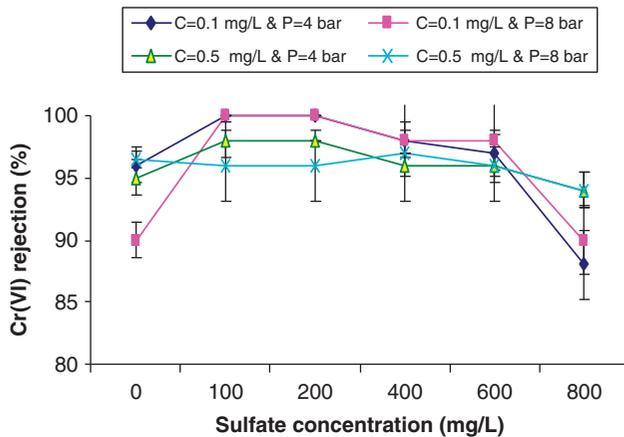


Figure 5 | Cr (VI) rejection as a function of TMP in various concentration of sulfate.

sulfate (0.23 nm) (Košutić et al. 2004) is larger than that of chromium (0.14 nm) (Yoon et al. 2009). In fact, Cr (VI) rejection is drastically reduced due to the effect on the reduced electric double layer (up to 600 mg/l) caused by increased concentrations of sulfate when some concentration accumulation occurs (Yoon et al. 2009). Due to sulfate concentrations of 400 mg/l in synthetic water, the simultaneous rejection of Cr (VI) and sulfate were done from 2 to 10 bar in concentrations ranging from 0.1 to 0.5 mg/l for Cr (VI) and sulfate for 400 mg/l (Figures 6 and 7).

Figure 6 shows that the rejection of Cr (VI) decreased with increasing chromium concentration. As can be seen, the rejection of Cr (VI) increased particularly for lower concentrations with the increase of TMP from 2 to 6, and remained unchanged for both concentrations of 0.1 and 0.5 mg/l. Therefore, the rejection of Cr (VI) in low concentrations appears to be based on Donnan exclusion and is therefore less influenced by pressure increases. In other words, greater

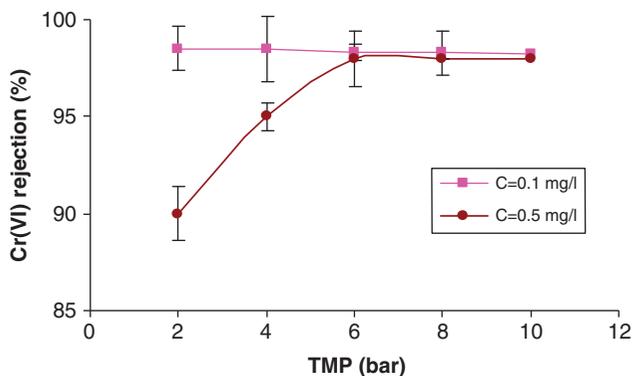


Figure 6 | Cr (VI) rejection as a function of TMP in presence of sulfate C=400 mg/l.

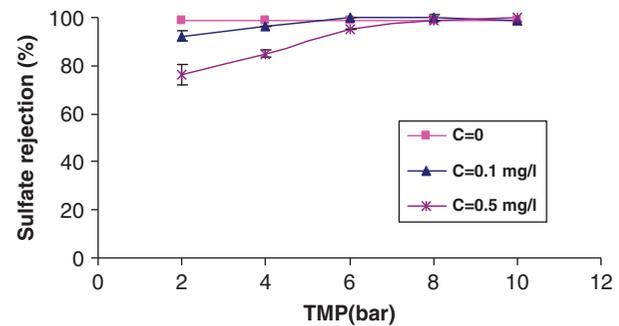


Figure 7 | Sulfate rejection as a function of TMP in various concentration of Cr (VI) C sulfate = 400 mg/l.

exclusion at low ion concentration (0.5 mg/l) was done effectively by the surface charge of NF. In addition, as previously discussed, Cr (VI) rejection is reduced due to the effect on the reduced electric double layer by the increased concentration of other ions, K^+ , Na^+ , and Mg^{+2} , when some concentration accumulation occurs (Yoon et al. 2009). A mass balance analysis (Table 3) confirmed these results. Figures 6 and 7 demonstrate that concentration polarization can hinder back diffusion of Cr (VI) (Figures 5 and 6) and sulfate (Figure 7) into the bulk solution, hence causing Cr (VI) and sulfate to accumulate near the membrane surface. This enhanced concentration polarization resulted in a greater concentration gradient of both Cr (VI) and sulfate, and it subsequently caused a decrease of Cr (VI) and sulfate rejection.

The results in Table 3 show that rejections for all ions were above 94%. On the other hand, NF90 achieved high rejection ($R > 94\%$) for all monovalent and divalent anions and cations (Krieg et al. 2004). The obtained permeate had a Cr (VI) level of 0.005 mg/l, which is on the lower of the established MCLs spectrum (WHO 2008). However, the rejection of Cr (VI) in Birjand water (94%) (Table 3) was less than in synthetic water (97%) (Figures 2 and 3). It appears that this reduction of Cr (VI) rejection was due to the effect of the reduced electric double layer caused by the increased concentration of positive ions such as Ca^{+2} , Na^+ , and Mg^{+2} .

Table 3 also indicates that, except for chloride, accumulations of other ions, such as SO_4^{-2} , Mg^{+2} , Ca^{+2} , Cr^{+6} , and Na^+ (which can be called TDS), on NF were above 50%, and therefore, chloride had only a small impact on the repulsion of co-ions (especially for chromate and sulfate).

Table 3 | Mass balance analysis (MBA) in Birjand drinking water at 4 bar

Parameter MBA	Cr(VI)	SO ₄ ²⁻	Ca ²⁺ as CaCO ₃	Mg ²⁺ as CaCO ₃	Cl ⁻	Na ⁺	TDS
Concentration (mg/l)	0.1	390	100	314.5	240	230	1120
Rejection (%)	94.3	99.5	100	100	96	98.7	99.1
In permeate (%)	5.19	0.54	0	0	4	1.3	1.05
In concentrate (%)	10.38	47.29	30.05	22.16	85.65	45.65	14.24
On nanofilter (%)	84.43	52.17	69.95	77.84	10.35	53.05	84.86

CONCLUSIONS

In the present study, the possibility of using NF for the removal of chromium, a toxic inorganic, from brackish (as Birjand drinking water) groundwater by NF was investigated. The results indicated that the addition of TDS in feed solutions, driven pressure, and pH all have a significant effect on Cr (VI) rejection by NF. In comparison, the influence of ionic strength as well as Cr (VI) concentration was found to be less important. In view of human health effects, our findings revealed that NF technology is efficient, and therefore applicable, for the removal of Cr (VI) and sulfate from Birjand drinking water.

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