

Removal of Hexavalent Chromium and Total Dissolved Solids from Water Using Nanofiltration

B. Barikbin¹⁺, Bagher Mortazavi² and Gholamreza Moussavi²

¹Family Health and Environment Research Center, Birjand University of Medical Sciences, Birjand, Iran

²Department of Environmental Health, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran

Abstract. The removal of Cr (VI) and some dissolved solids from water using nanofiltration was investigated. The effects of operating pressures were investigated for a pressure range of 2 to 10 bar in concentrations ranging from 0.1 to 0.5 mg/l for Cr (VI) and 500 to 2500 mg/l for total dissolved solids were the same as the levels found in water sources. 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⁻¹ and no significant effect between 4 and 8 bar in 0.5 mg.L⁻¹ concentrations. The simultaneous rejection of dissolved solids and Cr (VI) (varying from 90% to 99.9%) showed that the influences of the ionic strength of a mixed aqueous solution were found to be weak at the selected concentrations of Cr (VI). Finally, a mass balance analysis was developed under optimal experimental conditions.

Keywords: Nanofiltration; Hexavalent chromium; Total dissolved solids; Rejection

1. Introduction

Some groundwater sources for drinking purposes due to the geological situation and/or anthropogenic contamination through discharging industrial effluents contain an increased concentration of ions such as hexavalent chromium as well as some other dissolved components in the upper value of the established MCL_s. Cr (VI) is an oxyanion known to cause various health effects such as allergic reactions, skin rashes, lung cancer, kidney and liver damage and etc [1]. According to the WHO standards, a risk-based drinking water standard of 50µg L⁻¹ has been established for Cr (VI) [1]. Due to its high toxicity, the standard concentrations of Cr (VI) in drinking waters must be strictly controlled. For TDS, although its health effects are relatively short-term, it is clear that water with the sulfate level exceeding 1000 mgL⁻¹ should not be used long term[8]. The presence of high levels of TDS may also be objectionable to consumers, owing to excessive scaling in water pipes, heaters, boilers and household appliances. No health based guidelines value for TDS has been proposed. To prevent health effects, chromium and TDS which often are simultaneously present in groundwater, required to be removed from drinking water before distributing the between the consumers. Due to developing the membrane production technology, extensive attention has been pulled in recent years on the application of membrane technology for water treatment [5]. Simultaneous removal of Cr (VI) and sulfate by NF as a membrane method have difficulties in practice. But when two or more of the mentioned parameters are to be removed, NF is cheaper than the combination of two conventional techniques such as chemical precipitation and ion exchange or activated carbon [6,7]. Many researchers have used NF to remove sulfate or chromium individually from water [2, 3, 8, 10, 11, and 12]. They have investigated the influence of physicochemical behavior [3] and pH [4] on NF. To the best of our knowledge from available literature on NF, no report could be found neither on Cr (VI) removal at low level, nor on simultaneous removal of Cr (VI) and TDS from contaminated drinking water. Therefore the main purpose of

⁺ Corresponding E-mail: b_barikbin@yahoo.com;

the present work is the investigation of behavior of NF for simultaneous removal of Cr (VI) and TDS from water. To perform this, the effect of the most important effecting parameter, i. e. pressure, pH, permeate flux, and concentration was evaluated on the removal of mentioned contaminant using NF.

2. Material and Methods

All the experiments were carried out in a pilot scale membrane unit made of stainless steel equipped with one polyamide spiral-wound membrane type NF90 (Film Tec Corporation).

The system was made dead-end filtration, when filter rinsing was required, by closing the concentrate valve and only allowing the fluid to pass through the membrane. Characteristics of the studied membrane have been shown in Table 1.

Table 1: Main Characteristics of the used membrane

Parameter	NF90-4040
type	Polyamide Thin-Film Composite
Configuration	spiral wound
Membrane area, m ²	7.6
Length, mm	1016
Diameter, mm	99
Permeate flow rate, m ³ /d	7.6
Max Operating Temperature, °C	45
pH Range, Continuous Operation	2-11

Samples of permeate were collected after 15 minutes of filtration. The parameter take 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)

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

pure water flux

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

permeate flux

$$JV = VP / A.t \quad (3)$$

Where C_p and C_o were the concentration in permeate and in the feed solution, respectively; Jvp , L/h.m²; Jv , L/h.m²; V_{pw} = volume of pure water permeate collected per unit time t , L/h; Vp = volume of permeate collected per unit time t , L/h; and A = area of the membrane, m². After each test, the membrane were rinsed using 1% citric acid for 5 minutes (mixed with sodium hydroxide to obtain pH=4) and then pure water (10 min) in order to remove the scale. To demonstrate the fate of the rejected ions by membrane, the mass balance analysis was developed for the unit boundary, under the optimum experimental conditions. The instrument was operated at room temperature of $25 \pm 2^\circ\text{C}$.

All salts were purchased from Merck Corporation with purity over 99%. Concentration of Cr (VI) was analyzed by using UV-Vis spectrophotometer (Unico UV-2100) at 540 nm wave length by using 1, 5-diphenylcarbazide as a color complex agent based on procedure detailed in standard methods [9]. TDS was analyzed by both Gravimetric and Conductimetric Method [9]. All the prepared calibration curves were linear over the concentration range of 0-0.5 mg L⁻¹ (for Cr) and 500-2500 mg L⁻¹ (for TDS) with R^2 greater than 0.99. The adjustment of pH was made by using 1N NaOH and HCl by a pH meter (JENWAY 3505). To ensure repeatability of data, all experiments were conducted in duplicate and the averages of results were reported.

3. Results and Discussion

3.1. Effect of pH on Chromium Removal

Figure 1 represents the rejection of Cr (VI) from water as a function of pH at TMPs varying from 2 to 10 bars.

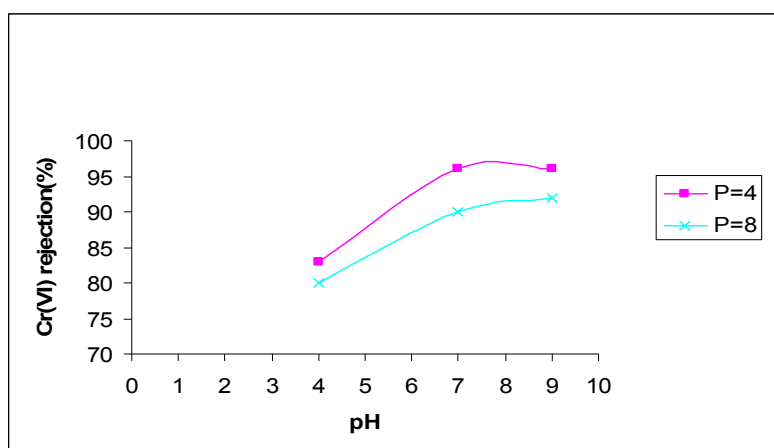


Fig. 1: Cr (VI) rejection versus pH at TMPs (temperature: 25oC and C=0.1mg/l)

Figure 1 shows that the rejection of Cr (VI) increased with the increase of pH at all pressures. It is clear that as the pH is increased, bivalent ions of chromium (CrO_4^{2-} / $\text{Cr}_2\text{O}_7^{2-}$) are formed and confirms the higher rejection in alkaline range with high efficiency [4]. Because of higher and lower rejection in 4 and 8 bars respectively, these two pressures have chosen for investigation at different salts mixtures in fixed Cr (VI) concentration. As seen in the Figure 1 rejection of Cr (VI) in each pH is increased with decreasing of pressure. For example in pH=7 the rejection percent of Cr^{+6} at 4 bars was averagely 7% higher than at 8 bars. This fact can be explained by passing the little size of Cr^{+6} (0.14 nm) [10] across the filter by increasing pressure. To demonstrate the fate of the rejected ions by membrane, a mass balance analysis was developed, under the best experimental conditions. Difference between feed concentrations of each parameter with sum total of permeates and concentrate made mass of component which is accumulated on nanofilter. Table 2 shows that pressure of 6 bar (100% removal of Cr^{+6} and 99.8% for TDS) can be considered for health points of view. But pressure of 10 bars can produce 81.8% and 84.63% concentrated Cr^{+6} and TDS in concentrate discharge line respectively. In addition, presence of 3.65% and 15.07% for Cr (VI) and TDS respectively on nanofilter can decrease of cleaning, prevent scaling and lower the required pressure. Therefore it can be significant for environmental friendly and cost benefit point of view.

Table 2: Mass balance analysis

Pressure	Feed Concentration (mg/l)			Mass balance analysis											
				Permeate rejection (%)			In Permeate (%)			In Concentrate (%)			On Nanofilter (%)		
	Cr (VI)	Sulfate	TDS	Cr rejection	Sulfate rejection	TDS rejection	Cr	Sulfate	TDS	Cr	Sulfate	TDS	Cr	Sulfate	TDS
2	0.1	500	2500	%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	2500	%100	%99.6	%99.7	0	0.43	0.24	0	20	21.9	100	79.56	77.85
6	0.1	500	2500	%100	%100	%99.8	0	0	0.29	0	2.96	7.03	100	97.03	92.66
8	0.1	500	2500	%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	2500	%86	%100	%99.7	14.54	0	0.28	81.8	97.32	84.63	3.65	2.67	15.07

Finally, we presented and explained the performance of NF membrane for simultaneous removal of chromium as a toxic inorganic and TDS ions from water. Results indicated that the hexavalent chromium and TDS in feed solutions, driven pressure and pH have significant effect on NF but influence of salt addition and ionic strength were found to be insignificant. Findings revealed that NF technology is a efficient and thus applicable for simultaneous removal of Cr (VI) and TDS from water.

4. Acknowledgements

The authors would like to acknowledge Tarbiat Modares University for their laboratory and technical support. The authors are also thankful to Birjand University of Medical Sciences and managing director of Birjand Water & Wastewater Corporation for water sampling and a financial grant.

5. References

- [1] Bartels, C., Wilf, M., Casey, W. & Campbell, J. 2008 New generation of low fouling nanofiltration membranes. *Desalination* **221** (1-3) 158-167.
- [2] Boussu, K., Vandecasteele, C. & Van der Bruggen, B. 2008 Relation between membrane characteristics and performance in nanofiltration. *J. Membr. Sci.* **310**(1-2), 51-65.
- [3] Hafiane, A., Lemordant, D. & Dhahbi, M. 2000 Removal of hexavalent chromium by nanofiltration. *Desalination* **130** (3), 305-312.
- [4] Haghsheno, R., Mohebbi, A. Hashemipour, H. & Sarrafi, A. 2009 Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin. *J. Hazard. Mater.* **166** (2-3), 961-966.
- [5] Hilal, N., Al-Zoubi, H., Darwish, N. A., Mohammad, A. & AbuArabi M. 2004 A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modeling, and atomic force microscopy. *Desalination* **170**(4), 281-308.
- [6] Krieg, H.M., Modise, S.J., Keizer, K. & Neomagus, H.W.J.P. 2004 Salt rejection in nanofiltration for single and binary salt mixtures in view of sulfate removal. *Desalination* **171**(2), 205-214.
- [7] Košutić, K., Novak, I., Sipos, L. & Kunst, B. 2004 Removal of sulfates and other inorganics from potable water by nanofiltration membranes of characterized porosity. *Sep. Purif. Technol.* **37**(3), 177-185.
- [8] Muthukrishnan, M. & Guha, B.K. 2008 Effect of pH on rejection of hexavalent chromium by nanofiltration. *Desalination* **219**(1-3), 171-178.
- [9] Standard Methods for the Examination of Water and WasteWater (2005). 21th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- [10] Taleb-Ahmed, M., Taha, S., Maachi, R. & Dorange, G. 2002 The influence of physico-chemistry on the retention of chromium ions during nanofiltration. *Desalination* **145**(1-3), 103-108.