Evaluation and Comparison of Sulfate Anions Removal from Artificial and Industrial Wastewaters by Nanofiltration Process in a Laboratory Scale

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Abstract: In this study, the performance of a nanofiltration process in sulfate anion reduction from artificial and industrial wastewaters was investigated. For this purpose, the effects of pressure, temperature, and volume flow rate and sulfate concentration of feed were studied. In order to prepare artificial wastewater (i.e. Sodium Sulfate) and to adjust the pH of the feed, both Sodium Hydroxide and Acetic Acid were used. The concentration of sulfate in the artificial wastewater was in the range of the industrial one (i.e. 400~500 ppm) and the pressure range, which had the most important influence on retention, was between 138~552kPa. In order to organize the experiments and obtain a specific procedure to perform the required tests, Minintab 16 software has been utilizes. The results showed that the reduction of sulfate anions, which had bivalent charge with big molecule size, occurred at high level of 96~99%. Higher pressure and temperature led to increase in this retention rate, while it reduced at high level of sulfate concentration in the feed. The condition in which the pressure, temperature, and feed flow rate were respectively 50345 kPa, 25ºCand 4L/min were indicated as the optimum condition.

Keywords: Sulfate anion, Industrial wastewater, Nanofiltration, Removal.

1. INTRODUCTION

In last few decades, oil was regarded as the most important wealth of countries, however, it is highly expected that in near future, water will be exchanged with oil, since there are numerous alternative sources of energy such as gas, nuclear energy, solar energy and so forth. But when it comes to water, there is only one option which is just water. Hence, a great deal of time and effort has been invested to economize water resources using different methods among which wastewater treatment has attracted the attention of many researchers in recent years. Two third of the Earth is overlaid by water and almost all substances are soluble in water, the solubility of which appertains to different parameters such as temperature, pressure, pH, chemical potential and partial concentration of other substances. These impurities are categorized as suspended solids, gases, and dissolved solids [1].

In recent years, strict limitations have been placed on industrial wastewaters. However, in such restrictions, not much attention has been paid to the issues related to dissolved sulfate [2]. The damage caused by sulfate emissions is not direct, since sulfate is a chemically inert, non-volatile, and non-toxic compound. Sulfate anions are discharged into the aquatic environment in wastes from industries which use sulfates and sulfuric acid, such as mining and smelting operations, kraft pulp and so forth. High sulfate concentrations as well as low pH conditions can cause various environmental and health related problems. The cations accompanied by sulfate are categorized into two types; soluble like Na^+, K^+, Mg^{2+}, and insoluble like Ca^{2+}, Ba^{2+} [3].

Sulfate is one of the least toxic anions with a lethal dosage for human of 45g as potassium or zinc salt; in such case, it is questionable as to whether toxicity is associated with the sulfate or the counter ions. The reported minimum dosage of magnesium sulfate in mammals is 200mg/kg. People consuming drinking water containing sulfate in concentrations exceeding 600mg/L commonly experience cathartic effects; resulting in purgation of the alimentary canal [4].

High concentration of this anion in industrial waters and wastewaters can lead to several problems as follows; scaling production in heat exchangers and boilers is resulted in by sulfate. At low pH conditions, sulfates absorb protons, which cause corrosion on transmission systems. Such problem could be overcome by adding $Ca(OH)_2$, which increases pH. However, despite pH increasing, the wastewater will be saturated by $CaSO_4$and high concentrations of $CaSO_4$ in water reduce production and damages equipment [5]. In sum, sulfates removal from effluents is essential

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for; a) prevention of salination of surface water, b) prevention of scaling, c) prevention of bio-corrosion, d) prevention of acid corrosion [4].

There are various processes for treatment of sulfate laden waters including chemical treatment, semi-permeable membranes, ion-exchange, biological mechanisms and so forth. Chemical treatment processes with mineral precipitation are generally the least expensive but produce the largest amounts of waste. Biological sulfate reduction has an additional advantage of removing trace metals from the mine water. For the removal of sulfate from mine water, the lime/limestone process, GYP-CIX as an ion-exchange process, and biological sulfate reduction in a bioreactor are the most suitable processes [4].

In the past, sulfate was removed by Barium Carbonate. Kun [6] studied the removal of sulfate with Barium Carbonate and despite obtaining good results, he identified three problems: 1) a long retention time requirement, 2) high concentration of soluble Barium in the treated water when more Barium Carbonate was dosed than stoichiometrically required, 3) and the last one was the high cost of the Barium Carbonate. Volman [6] overcame the cost problem by demonstrating that Barium Sulfate could be recovered and reduced efficiently and economically with coal under thermal conditions to produce Barium Sulfide. Wilsenach [6] demonstrated the economic viability by calculating the cost of producing Barium Sulfide from Barium Sulfate. Trusler *et al*. [6] developed a barium carbonate method using a two-stage fluidized bed reactor system to overcome the long retention time and the high barium concentration in the treated water.

Košutić *et al*. [7] surveyed the removal of sulfate and other inorganic compound from drinking waters by nanofiltration experiments in Prud (Croatia). Their results have shown very high retentions of sulfates (more than 97%).

International Network for Acid Prevention (INAP) institute [4] studied sulfate removal from industrial wastewaters. They selected several processes to reach this purpose. Table **1** summarizes the results of this study. The selection criteria for each process were based on: (1) applicability to sulfate removal, and (2) availability of data on sulfate removal and costs. All the experiments have been performed for mine water of Sceunda coal mine near Johannesburg in South Africa. The mine water was characterized by high TDS (4g/L) and sulfate (2.2g/L) concentrations and pH=8.4. Tubular Reverse Osmosis (TRO) pilot plant was investigated by them. Over the test period of 1800 hrs, the average salt rejection was 96%. A decrease in standard flux of 5% or an increase of 10% in operating pressure was a sign that the membranes needed to be cleaned. It was reported that after every 350 hrs of operation, the membranes should be cleaned, to restore the flux.

Aleixandre *et al*. [8] carried out an evaluation of sulfate concentrations in the different residual streams of a tannery. Tannery industries generate wastewater containing high concentrations of sulfates. In the pickling process, the presence of sulfates is due to the Sulfuric acid added for pH lowering, and Chromium is used as $Cr_2(SO_4)$ in the tanning process. Concentrations higher than 2000 mg/L were usual in tannery wastewater, and the legal standard was 1000 mg/L at the beginning of 2005 in Catalonia (Spain). Sulfate reduction of more than 90% was achieved, and also permeate quality was reported to be good enough to be reused.

Benatti *et al*. [9] investigated Barium and Calcium precipitation of sulfate from mixed waste chemicals and the effect of the wastewater composition on the sulfate precipitation. The results showed that at the concentration of 80 g/L, Barium precipitation achieved a sulfate removal up to 61.4% while Calcium precipitation provided over 99% sulfate removal. The precipitate characterization showed chemical compositions with no toxic risks that favored its reuse in innumerous processes applications.

Tait *et al*. [10] studied sulfate removal by crystallization. Batch experiments on a landfill

Table 1: INAP's Sulfate Reduction Methods [4]

Proposed methods	Feed Concentration (ppm)	Product Concentration (ppm)	Retention
Mineral Precipitation	3000	1219	59.37
Ion-exchange	649	69	89.73
Reverse Osmosis	1149	113	90.16
Biological treatment	8342	198	97.63

wastewater with a similar composition to other sulfate rich industrial wastewaters (high levels of organic and inorganic contaminants) were used. The results showed that Gypsum crystallization was an effective means for bulk removal of sulfate from highly contaminated wastewaters, but precipitation processes, therefore, could not economically reduce sulfate to very low levels. At an industrial scale, it was more economical to operate with crystal recycle than with manufactured seed only. Unfortunately, impurities in the wastewater substantially increased the solubility of gypsum and a substantial excess of calcium might be necessary to attain the desired level of sulfate removal.

Haghsheno *et al*. [11] studied sulfate removal from the Sarcheshmeh Copper Complex (Kerman province, Southeast of Iran) wastewater, by an anion exchange resin. Batch experiments of sulfate anions adsorption on Lewatit k6362 resin were carried out. The results of their study showed that maximum removal of sulfate anions takes place in the resin dosage of 1000 mg/100 ml, and with increasing the feed flow rate from 30 to 70 ml/min, the anionic content in the outlet stream of the column increased. In addition, other ions in the effluent caused much inconvenience and had adverse effects on system performance [2, 11]. Alizadeh *et al*. [12] researched sulfate removal from ABS plant wastewater by anaerobic biological treatment. The maximum sulfate removal percentage was 86% in an experimental setup. Possibility of using wastewater with no pre-treatment and no change in temperature was the advantages of this method. However, high corrosion characteristic of the microorganism, which was used in their study, was the major disadvantage. Although there are some studies on removal of sulfate anion form wastewaters, application of new technologies such as nanofiltration seems to be necessary, particularly for elimination of pollutants from industrial wastewaters.

In this study, sulfate removal by a nanofiltration process in a laboratory scale was carried out. To achieve this purpose, the effects of different independent parameters (i.e. pressure, temperature, volume flow rate and sulfate concentration of feed) on sulfate removal and permeate flux were investigated using artificial wastewater. Then optimum conditions of sulfate removal were obtained. To investigate the effects of other ions, which are present in industrial wastewater, on sulfate elimination and permeate flux, all tests, especially at optimum conditions, were repeated for the industrial wastewater.

2. NANOFILTRATION PROCESS

Nanofiltration is a kind of membrane processes, which is considered as a physical treatment (i.e. without occurrence of any chemical reaction) with pressure as the driving force. Membrane processes are categorized according to the smallest particles which pass the membrane; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Based on the size of particles passing the membrane and the operating pressure, NF is placed between UF and RO. These membranes also have selective separation of molecules and ions with high molecular weight. For instance, Sulfate (SO_4^{2-}), a bivalent anion with high molecular weight cannot pass whereas chloride anions (Cl^-) can pass [13].

Saving energy during separation process due to no change in phase and temperature between feed and product, being faster due to low thickness of membranes, which leads to fast mass transfer, being more efficient and less usage of solvents or chemical aids than other separation processes, no peril to environment, high flexibility in plant design and possibility of being combined with other separation processes, and simple technology can be mentioned as some advantages of membrane, which are used in different industries [14, 15].

2.1. Characteristics of Membrane Filtration

2.1.1. Permeability Coefficient

Permeability coefficient is the flux permeate stream on the unit pressure, which is defined as below:

$$L_p = \frac{J}{P_e} \tag{1}$$

where L_p is membrane permeability coefficient, P_e is effective pressure on the membrane, and J is permeate flux [15].

The relation between permeate of solute and operating pressure for pure solute is linear. According to Darcy's law, filtration flux depends on operating conditions, membrane characteristics and the fluid under filtration, i.e:

$$J = L_p \frac{\Delta P}{\mu} \tag{2}$$

where J is permeate flux, ΔP represents pressure difference along membrane or effective pressure on the membrane, and μ is solute dynamic viscosity [15].

If membrane permeability is considered as the initial hydraulic resistance of membrane, it will be shown as below:

$$J = \frac{\Delta P}{\mu . R_M} \tag{3}$$

where R_M is membrane initial hydraulic resistance expressed in terms of meter [15].

2.1.2. Retention

Retention (R) is a function of membrane's selectivity properties. It is calculated by the equation below:

$$R = 1 - \frac{C_p}{C_a} \tag{4}$$

where C_p is the concentration of specific element in filtrate (permeate), and C_a is the concentration of the element in feed [15].

Due to concentration polarization phenomenon, two retention terms as Intrinsic Retention and Observed Retention are used. Concentration polarization phenomenon is the accumulation of retained particles near the membrane surface, which causes the concentration difference between the feed solution (behind the membrane) and retained solution. Model of film theory is used to describe this phenomenon [15].

3. MATERIALS AND METHODS

3.1. Experimental Setup

Figure **1** shows the process flow diagram for the experimental setup used in this study in order to investigate the nanofiltration process efficiency. According to this figure, this setup is fully returned. It means that both permeate and concentrate outlets are turned back to the feed tank in order to avoid wasting the feed. Due to the nanofiltration mechanism, which is a type of physical removal processes, turning back the outlets is possible and has no significant effect on the results.

According to the process, which is fully returned, and due to the high pressure pump, the feed temperature raised almost 3°C during each experiment which took at least 30 minutes. In order to prevent this temperature increment, a cooling system similar a typical refrigerator system, was used. An electric heater was also used to adjust and control the feed temperature to assess the effect of temperature in the experiments. These cooling and heating systems shown as E-101 in Figure **1** were placed in the feed tank. As can be seen, there is a temperature control system (TIC) which indicates the feed temperature, compares it to the set point value and then signals to the heater/cooler in order to adjust the feed temperature.

F-101 refers to a microfiltration stage which is needed for bigger particles removal to protect nanofilter from fouling. It has two inner stages, 10 and 5 micron filters, which represents the pores size of the filters.

3.2. Characteristics of Nanofiltration Module

NF33-1812-50 was the trade mark of NF module, a spiral-wound module, with 1.8 4.6 cm. diameter, 30.5 cm. height, and capacity of 189L/day made by ASPRINN MEMBRANE, with FilmTec membranes. The

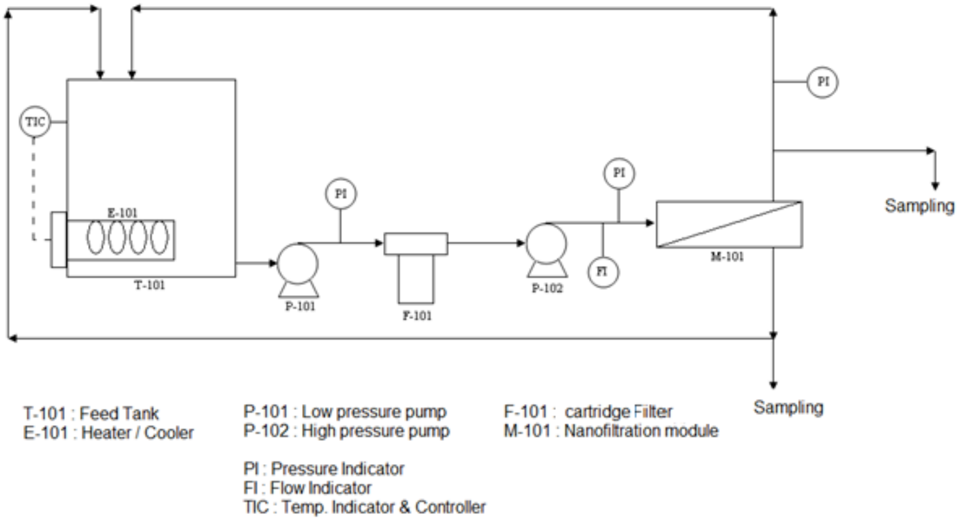
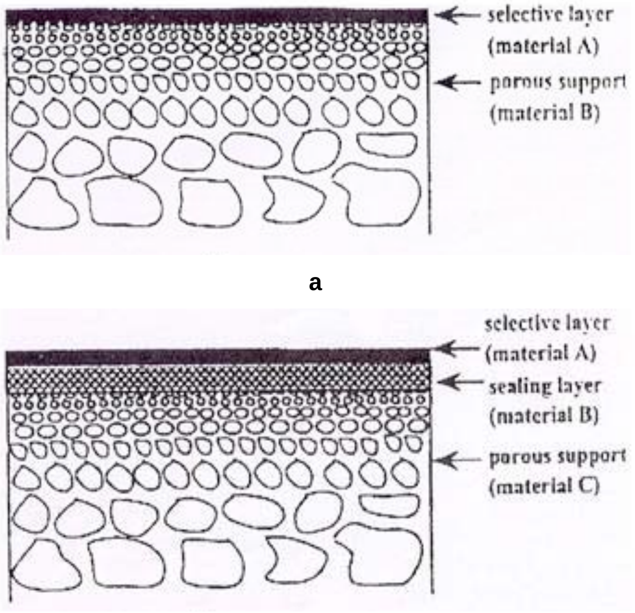


Figure 1: Laboratory setup flow diagram.

Table 2: Characteristics of NF33-1812-50 [16]

Membrane Type	Polyamide Thin-Film Composite
Maximum Operating Temperature	113°F (45°C)
Maximum Operating Pressure	600 psi (41 bar)
pH Range, Continuous Operation	2 - 11
Active area (m^2)	0.4255

main characteristics of this module are given in Table **2**. It was an asymmetric membrane with pore size gradient, an increasing in porosity from top to the bottom. Figure **2** shows the general scheme of the layers in this type of membrane. The separation characteristics of asymmetric membrane refer to the thin and compact layer, which is called selective layer [16].



a

b

Figure 2: Thin-Film composite membranes structure, **a**) single layer and **b**) multi-layer [15].

3.3. Sulfate Solutions

Stock solutions were prepared from several points of wastewater stream of Tehran Oil Refining Company. Sulfate ion concentration was found in the range of 400–500 ppm. The pH of these samples was approximately 7. Therefore, in all experiments the pH conditions were kept constant at 7. Metrohm 654 pH meter was used to measure the pH of the solution.

To measure sulfate anion concentration, ASTM D516-90 method, based on white precipitation of Barium Sulfate salt, was used. The spectrophotometer in this method was CamSpec, M350 Double Beam UV-Visible Spectrophotometer at 420 nm wavelength. A calibration curve based on SO_4^{2-} concentration (ppm) for standard solutions with known sulfate concentration versus adsorption was needed (see Figure **3**) [17].

The procedure of performing experiments at different conditions was designed by Minitab 16. Each experiment was performed at least twice at the same condition to ensure data repeatability. The precision of the measurements was mostly within 4%. First, all experiments were done with the artificial wastewater, then to investigate the effect of the presence of other ions on the sulfate removal, industrial wastewater from Tehran Oil Refining Company was used. In this study C_p, which is the sulfate concentration in permeate stream, and volume flow rate of permeate were measured.

4. RESULTS AND DISCUSSION

4.1. Effect of Pressure on the Sulfate Removal Rate

Figure **4** illustrates the effect of pressure on sulfate removal from the artificial wastewater for two feed inlet concentrations of 400 and 500 ppm. In this figure, each line was obtained for a constant temperature and feed volumetric flow rate. It was observed that increase in pressure from 138 to 552kPa, leads to increase in sulfate retention the rate of which is higher at lower pressures. According to the Spencer's study [18], increase in pressure leads to higher concentration polarization and consequently, higher sulfate retention. But there are some differences between our study and Spencer's work. First, the range of sulfate concentration of feed in that work was much higher and the trend of the variation of flux versus pressure was not linear, while linear trend (see Figure **6**) can be seen in this study. Hence, in this research, the concentration polarization phenomenon is negligible [18, 19], and it cannot be an appropriate explanation of retention's accretion. In order to clarify such increment, it can be mentioned that Na^+ cations which are present in both artificial and industrial wastewater have very small ionic

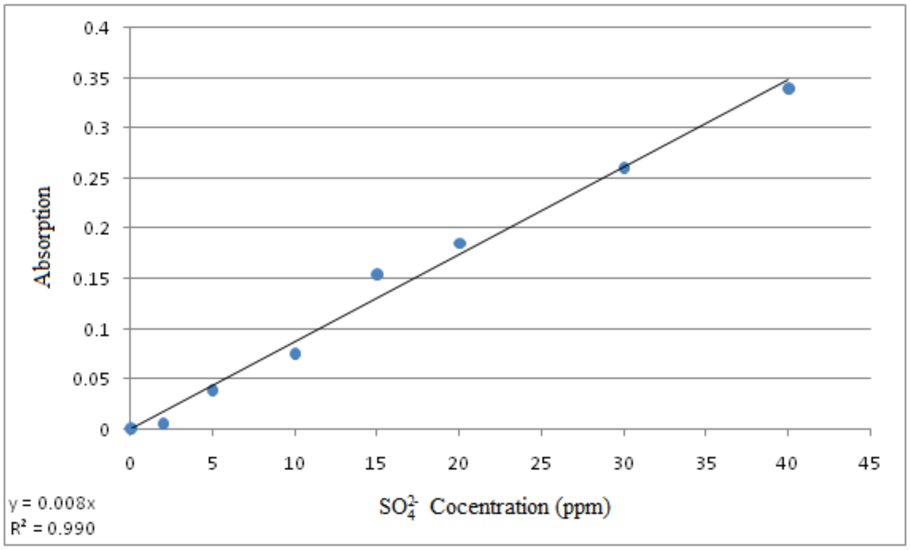
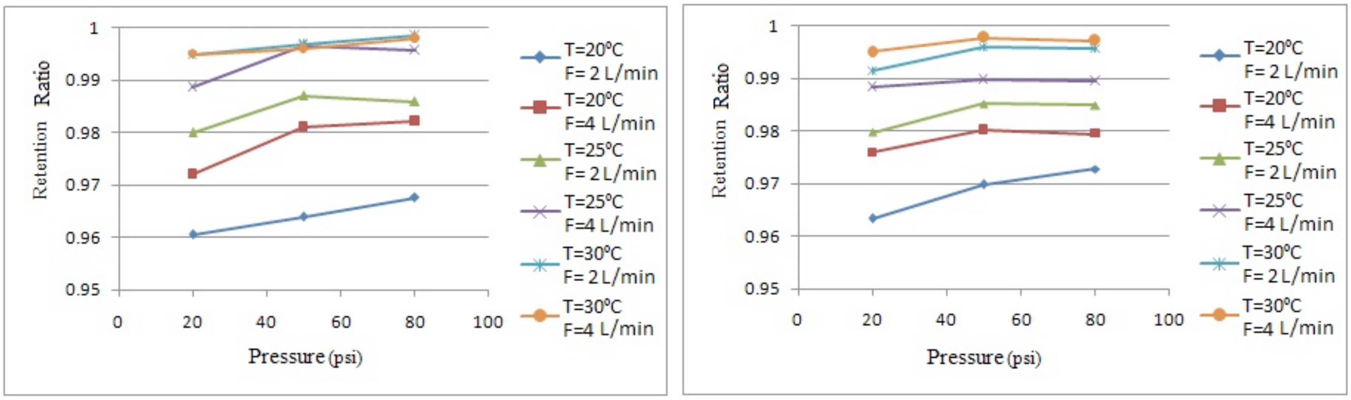


Figure 3: Calibration curve of sulfate concentration.



a **b**

Figure 4: Effect of pressure on sulfate retention (Artificial wastewater); **a**) Feed concentration; 400 ppm, **b**) Feed concentration; 500 ppm.

radii and low hydration energy (405 kJ/mol), and hence, they can enter the membrane pores, some of which remain in those pores leading to membrane surface resistance against the sulfate permeation [19].

Figure **5** shows the effect of pressure on sulfate removal from the industrial wastewater which contained 437.56 ppm of sulfate anion. Comparison between Figures **4** and **5** illustrates that sulfate retention for this case is lower than that for the artificial wastewater. This reduction is due to the existence of cations such as Ca^{2+} and Mg^{2+} in the industrial wastewater, which neutralizes negative sites on NF membrane surface and consequently, leads to higher permeation of sulfate.

NF membrane used in this study had negative surface charge which contributes SO_4^{2-} ions repelling. The resistance of the membrane against the fluid flow was constant, such that there were no significant differences in passing Na^+ and SO_4^{2-} by increasing the pressure. However, as pressure was increased above a certain value (e.g. about 335kPa), flux of solution detached the cations (Na^+), and hence, it would be possible for sulfate anions to pass through the NF membrane. However, in this study, this phenomenon is not sensible due to the high sulfate anions' size.

Figure **7** shows the effect of pressure on permeate flux for the industrial wastewater. From this figure, one can see that the permeate flux decreases in comparison with Figure **6** (i.e. artificial wastewater). It is caused by impurities and bigger-than-nano particles, which are present in the industrial wastewater. These contributions lead to increase in the membrane surface resistance against the passing stream and consequently, results in decrease in flux. Each line in

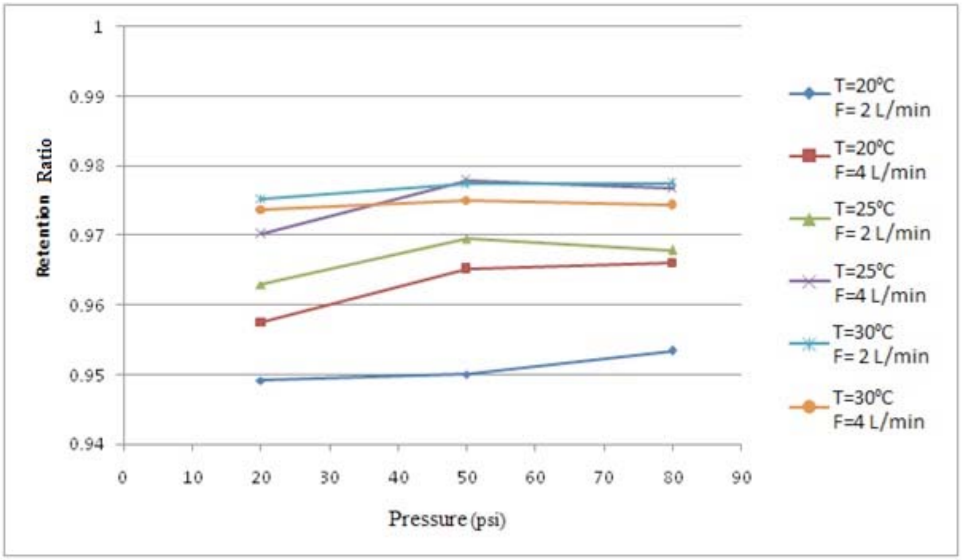
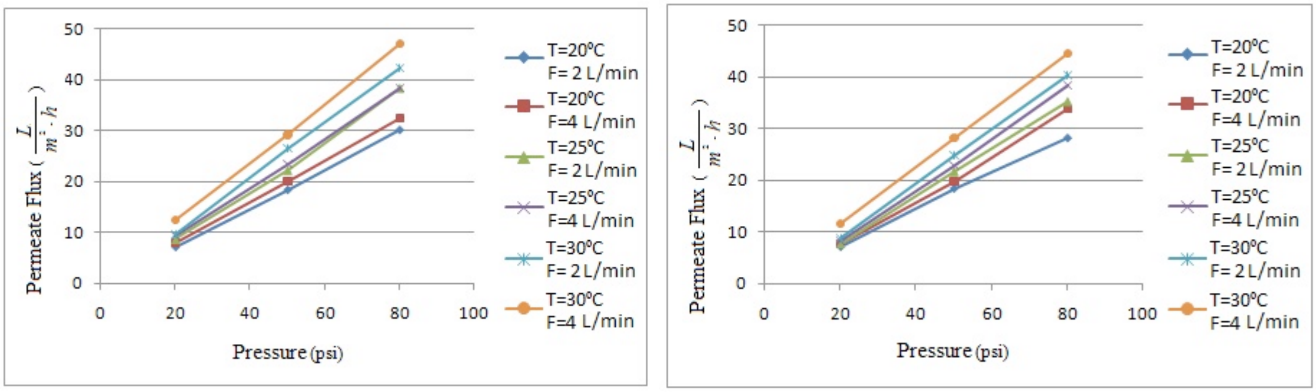


Figure 5: Effect of pressure on sulfate retention (Industrial wastewater).



a **b**

Figure 6: Effect of pressure on permeate flux (Artificial wastewater); **a**) Feed concentration; 400 ppm, **b**) Feed concentration; 500 ppm.

Figure **6** is related to the conditions of constant feed temperature and volume flow rate, and each sub-figure is related to a constant concentration.

4.2. Effect of Temperature on Sulfate Removal

The results of sulfate retention from the artificial wastewater, for different feed temperatures and two feed concentrations are shown in Figure **8**. In this figure, each line was obtained at constant pressure and feed volumetric flow rate and each sub-figure is only for a constant concentration. As one can see, increase in temperature from 20 to 30 ºC results in an increase in the retention due to higher solubility of salt (Na_2SO_4), lower probability of concentration polarization and preservation of membrane surface characteristic. According to these results, the temperature should be lower than the membranes endurance limitation to protect the performance of membrane. Figure **9** shows the effect of temperature on sulfate retention for the industrial wastewater. Comparing Figures **9** and **8**, one can see that the sulfate retention for the industrial wastewater is lower than that for the artificial wastewater. This behavior is similar to the effect of pressure on sulfate retention.

Figure **10** shows the effect of temperature on permeate flux for the artificial wastewater. This figure illustrates that the relation between permeate flux and temperature is almost linear. The reasons for the small observed deviation from linear trend are due to reduction of feed kinematic viscosity, osmotic pressure and increase in solution diffusion at higher temperature. Moreover, the results for the industrial wastewater are shown in Figure **11**.

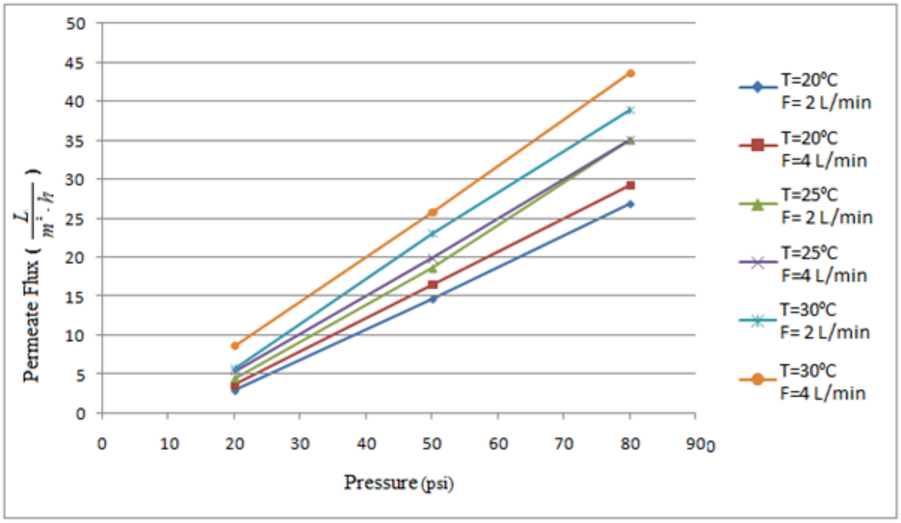
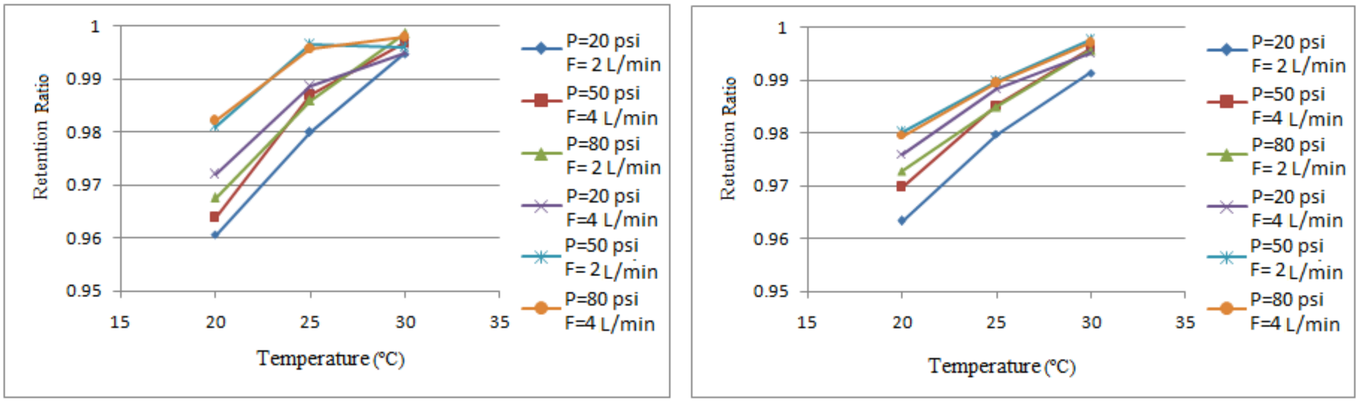


Figure 7: Effect of pressure on permeate flux (Industrial wastewater).



a **b**

Figure 8: Effect of temperature on sulfate retention (Artificial wastewater); **a**) Feed concentration; 400 ppm, **b**) Feed concentration; 500 ppm.

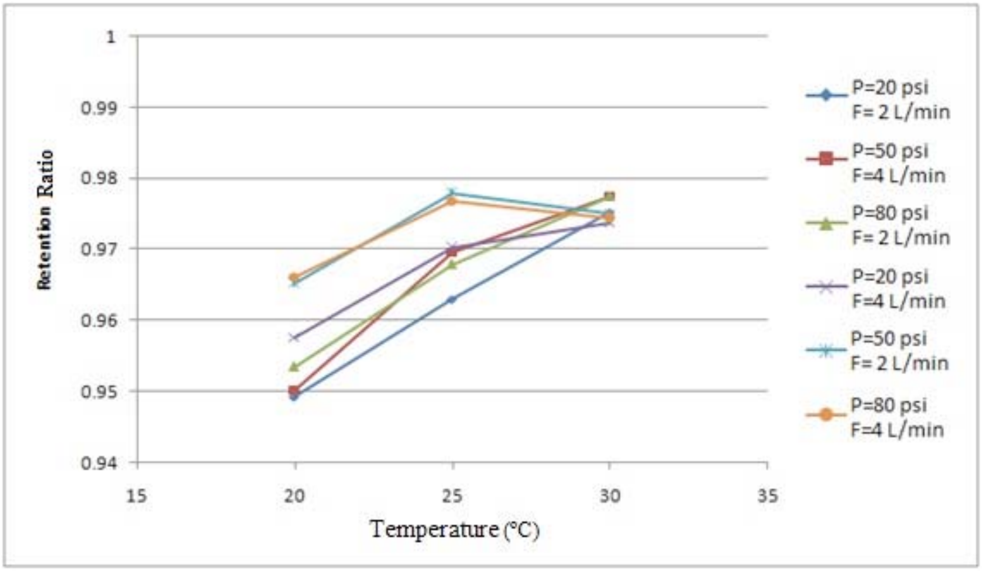
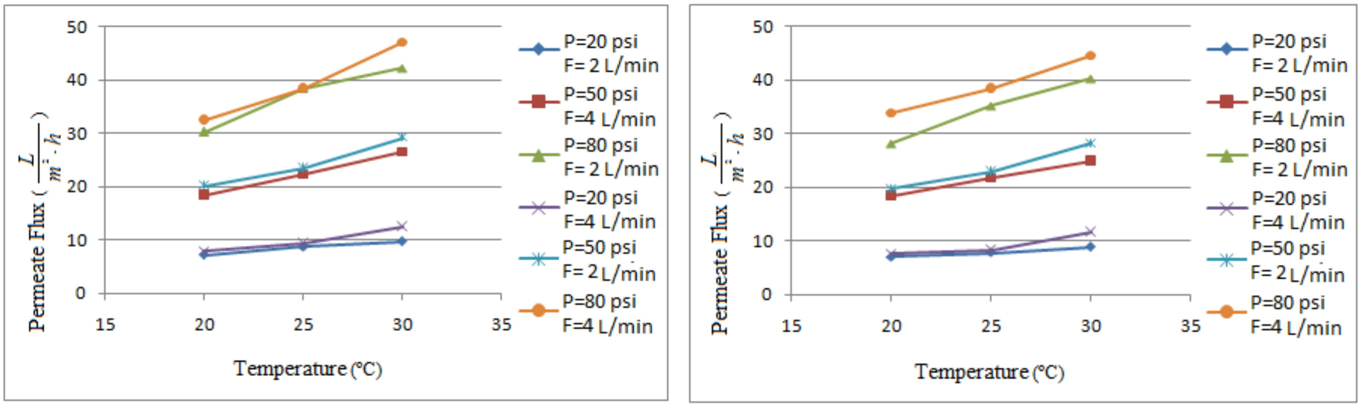


Figure 9: Effect of temperature on sulfate retention (Industrial wastewater).



a

b

Figure 10: Temperature effect on permeate flux (Artificial wastewater); **a**) Feed concentration; 400 ppm, **b**) Feed concentration; 500 ppm.

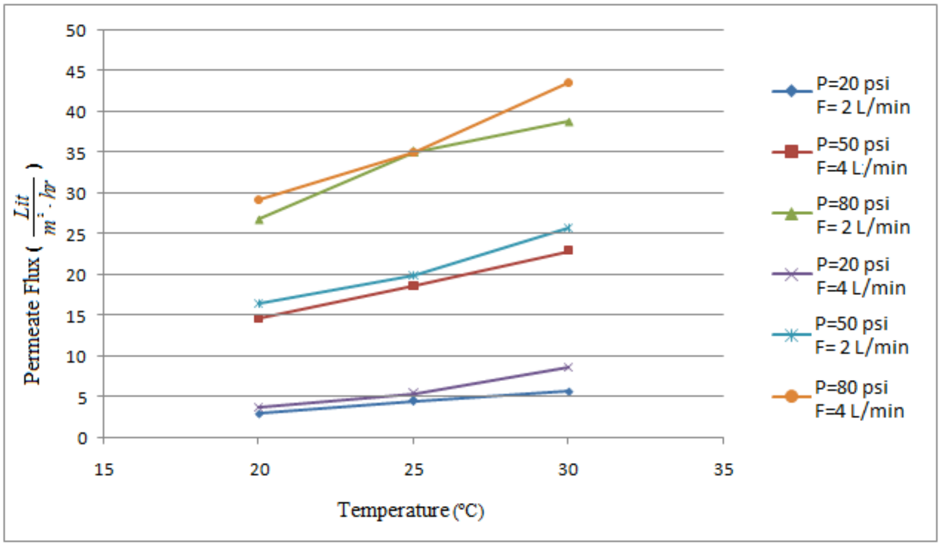


Figure 11: Temperature effect on permeate flux (Industrial wastewater).

4.3. Effect of Inlet Concentration

The two inlet concentrations considered in this study were 400 and 500 ppm. In this step, other parameters such as operating pressure, temperature, feed volume flow rate and pH were kept constant. As shown in Figure **12**, the effects of inlet concentration on sulfate retention depended depends on feed temperature such that from bottom to top, these effects are different. At low temperature (i.e. 20 ºC, bottom of the graph), increase in inlet concentration causes the sulfate retention to increase and at high temperature (i.e. 30 ºC, top of the graph) the situation is vice versa. In normal temperature (i.e. 25 ºC, middle of the graph), no sensitive change was observed in retention. In sum, increase in inlet concentration caused a decrease in sulfate retention. This is due to higher cations concentration, which decreases the negative sites on membrane surface and consequently, anions (SO_4^{2-}) can pass through the NF membrane. But the sulfate retention is still high because of its big size. It should be noted that in this figure and the following figures (i.e. Figures **13**, **14** and **15**), there are two points on each line, which have the same conditions except for concentration, and these conditions are shown in separate legends.

Figure **13** illustrates the inlet concentration effect on permeate flux. The results show that at higher inlet concentrations, the flux of permeate stream decreases. Higher solute concentration leads to membrane fouling and consequently, to a higher concentration polarization. This can be mentioned as a reason for flux decreasing which was more sensitive at higher temperature. With regard to industrial wastewater concentration, which is not always at constant level, it

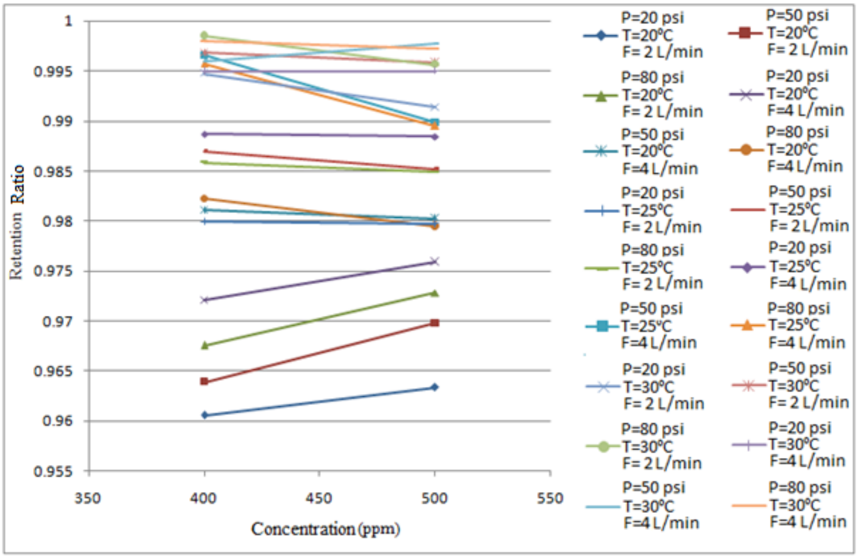


Figure 12: Effect of inlet concentration on sulfate retention (From bottom to top temperature increases).

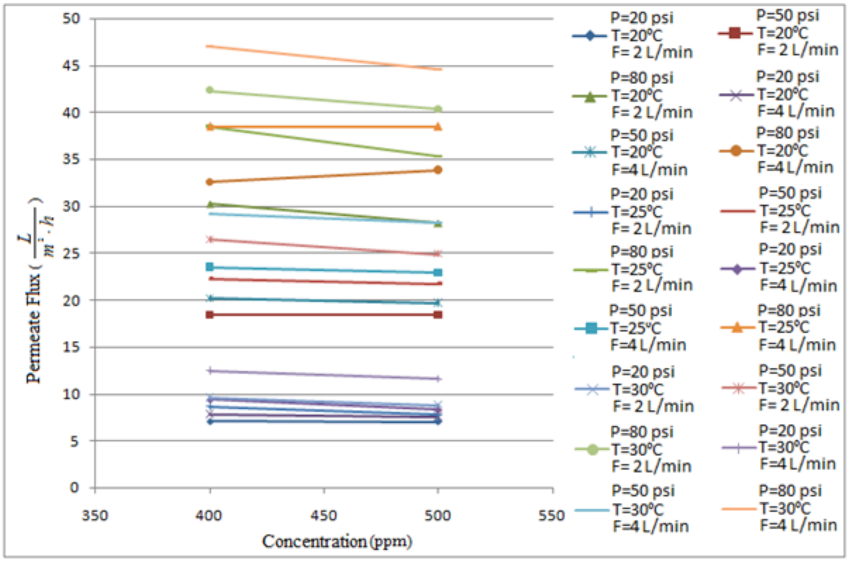


Figure 13: Effect of inlet concentration on permeate flux (From bottom to top temperature increases).

can be concluded that the feed temperature should be kept at the range in which the concentration effects can be neglected.

4.4. Effect of Feed Volumetric Flow Rate

The effect of feed volumetric flow rate on the sulfate retention is shown in Figure **14**. The results show that sulfate retention increases by increasing flow rate from 2 to 4 L/min. This is due to the reduction in concentration polarization and less accumulation of cations behind the NF membrane, since the residence time of concentrate before the membrane decreases. Therefore, the membrane preserves its surface charge, which results in higher sulfate retention.

The scale upon the NF membrane, acts as a hindrance against permeation. High ervelocity of the feed over the membrane can remove this scale and also entails thinner boundary layer adjacent to the NF membrane. Hence, the permeate flux will increase (see Figure **15**).

4.5. Optimum Conditions

To determine the optimum conditions, the process costs and conditions should be surveyed. In this study, the sulfate retention increased by increasing effective pressure upon the membrane. But its rate was not sensitive at higher level, and the operation costs will increase much higher due to higher energy

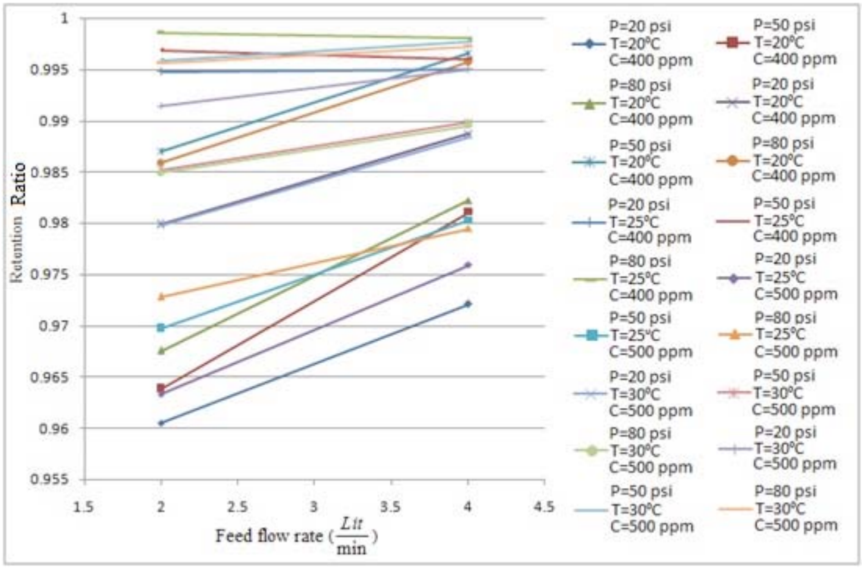


Figure 14: Effect of feed volumetric flow rate on sulfate retention.

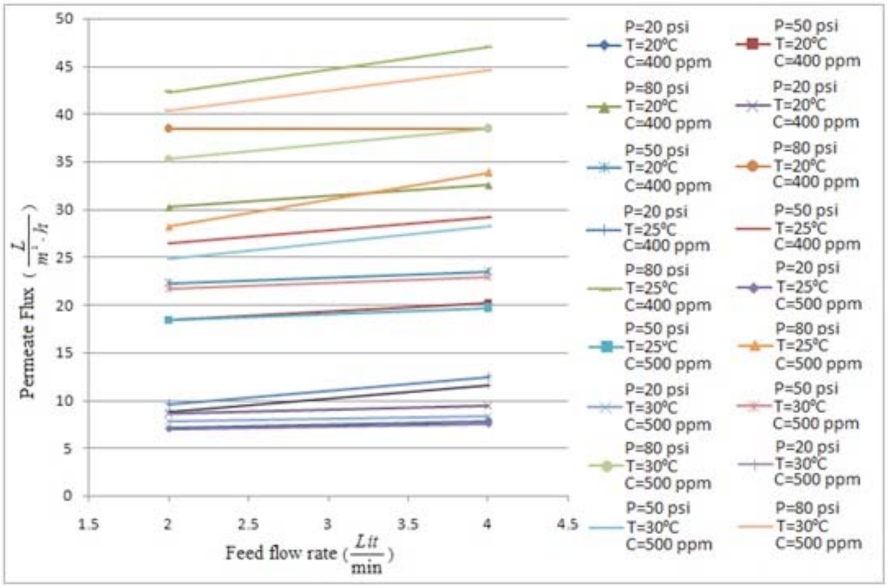


Figure 15: Effect of feed volumetric flow rate on permeate flux.

consumption at higher pressure. According to Figure **4**, the optimum pressure was 335kPa, the point that the low variation of sulfate retention against high pressure variation begins.

According to the relation between the effects of temperature and concentration on the sulfate retention, and concentration variation in industrial wastewater, both temperature and concentration should be analyzed simultaneously. For instance, increase in temperature causes a proportionate increase in sulfate retention, but at a high temperature (i.e. 30 ºC) and a high concentration (i.e. 500 ppm), the retention rate decreases. Hence, a value of temperature should be selected such that the variation of concentration can be neglected. Consequently, in this study, the temperature of 25 ºC was selected as the optimum one.

Higher inlet volume flow rate leads to higher sulfate retention as well as a higher permeate flux. But the capacity of NF module and of course the endurance of NF membrane should be noticed, which are given in the data sheet. In this study, 4 L/min of feed flow rate was selected as the optimum volume flow rate, which is lower than maximum module capacity (i.e. 7.6 L/min). At these optimum conditions the experiments were performed on an industrial wastewater to investigate the effects of other ions which exist in the wastewater.

Table 3: Analysis of Tehran Oil Refining Company Wastewater on May 21, 2011

	Before treatment	After treatment	Removal percentage (%)
Turbidity (NTU)	156	0.3	99.80
SO_4^{2-} (ppm)	437.56	11.624	97.34
NH_3 (ppm)	3.7	0.2	94.59
NO_3^- (ppm)	43.3	28.5	34.18
TDS [a] (ppm)	1160	480	58.62
TSS [b] (ppm)	10	2	80.00
Mg^{2+} (ppm)	32	17	46.87
Ca^{2+} (ppm)	148	28	81.08

[a] Total Dissolved Solid.
[b] Total Suspended Solid.

4.6. Industrial Wastewaterat Optimum Conditions

The analysis of important ions in the wastewater of Tehran Oil Refining Company is given in Table **3**, before and after treatment. The results showed that sulfate retention was 97.34% for the industrial wastewater, while this value was 99.66% for the artificial one and it is still high. Hence, in this study, it can be concluded that the quality of wastewater has no considerable effects on sulfate retention. The difficulty of sulfate passing through the NF membrane can be justified due to its charge (bivalent), large ionic size, and high hydration energy (1138 kJ/mol). But for monovalent ions like nitrate (NO_3^-), the ionic quality of the feed affects their retentions. For example, an increase in bivalent ions like sulfate, causes a considerable reduction in the nitrate removal [18]. As one can see in Table **3**, nitrate removal percentage is only 34.18. However, this NF membrane can remove at least 60% of NO_3^- In order to reach this rate of elimination for NO_3^- in this study, an extra NF stage is needed, which is placed directly after the first one for sulfate, due to low ionic content of permeate flow at the first stage.

Comparing the flux of permeates for the industrial and artificial wastewaters (i.e. 19.8 L/m^2.hr vs. 23.5 L/m^2.hr) shows a reduction in industrial one. This was due to existence of other ions like nitrate and TDS at high level, which caused some fouling upon the surface of NF membrane and hence, the flux of permeate decreased.

According to Figures **4** to **15**, it can be seen that there are not any major differences in trends of the graphs (i.e. linear, ascending, descending…), between industrial and artificial wastewaters. The solely difference is the numerical value. In other words, for the retention, there were about 1 to 2.35% reduction and for the flux, this value was about 3.52 to 4.43 L/m^2.hr. These numerical value differences are due to the existence of cations (i.e. Mg^{2+} and Ca^{2+}) and high impurities in the industrial wastewater. The former causes a decrease in surface negative charge of NF membrane and the latter causes some fouling in the NF membrane pores.

5. CONCLUSIONS

Although the presence of elevated sulfate anion concentration in industrial effluent is a major environmental concern, it can be remediated with the help of various existing sulfate treatment processes. In this study, the removal of sulfate anion was investigated from artificial and industrial (Tehran Oil Refining Company) wastewaters by nanofiltration process. The results showed that NF90 membrane could efficiently reduce sulfate anions concentration in range of 400–500 ppm. The removal of sulfate ions using a nanofiltration process depended on the effective pressure upon the NF membrane, the feed temperature and the inlet volume flow rate. Moreover, the following conclusions were drawn from the results of this study:

1) At higher operating pressure, not more than membrane durability, sulfate concentration in permeates stream and also flux of permeate increased rapidly in comparison with lower pressure.

2) For higher temperature, sulfate retention increased but with higher inlet concentration, the value decreased and there was some relation between temperature and concentration. Also

there is a limitation due to membrane endurance which should be taken into account.

3) As the volume flow rate was increased up to its limit (i.e. membrane endurance and module capacity), sulfate retention and flux of permeate increased.

Sulfate removals for the artificial and industrial wastewaters were 99.66% and 97.34%, respectively. The existence of other ions such as NO_3^-, TDS and so forth in the industrial wastewater led to a reduction in negative sites on membrane surface and a change in electrical balance on both sides of it, and consequently, the retention was lower for industrial wastewater. In this case, the pH of the solution affected the NF membrane surface charge, as it was not constant in the industrial wastewater. Therefore, detailed studies would be needed to investigate the effect of pH on sulfate removal by NF process.

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