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Sulfate removal from chlor-alkali brine using nanofiltration: Parameters investigation and optimization via Taguchi design method

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ABSTRACT

This work was aimed to optimize and investigate the effects of pH, temperature, pressure, feed flow rate, and concentrations of NaCl and Na_2SO_4 on retention of sulfate (SO_4^{2-}) and chloride (Cl^-) as well as permeate flow rate in almost saturated chlor-alkali brine nanofiltration (NF). For this purposes, a NF commercial membrane named NF-3 (Sepro) was used. The main goals of the current separation process were maximum and minimum retention of SO_4^{2-} and Cl^-, respectively, along with higher possible permeate flow rate. Based on Taguchi design method, a number of 16 trials with different levels of variations were considered as follows: temperature (27, 45°C), pressure (5, 9 bar), feed flow rate (180, 360 mL/min), NaCl concentration (25, 50, 100, 225 g/L), and Na_2SO_4 concentration (1, 7, 15, 25 g/L). Using mean of means and S/N ratio diagrams, the impact of each factor on NF process were studied. Analysis of variance (ANOVA) was also performed to determine the significance of each factor. The obtained results showed that SO_4^{2-} and Cl^- retentions were ranging 86.3%–93.4% and 26.7%–45.6%, respectively. Moreover, the permeate flow rate was obtained in the range from 0.24 to 2.44 mL/min for the flat sheet membrane with specific area of 112 cm². Finally, the effect of pH on separation performance and also chlorate (ClO_3^-) removal were investigated separately.

Keywords: Nanofiltration; Chlor-alkali brine; Taguchi; Sulfate retention; Highly concentrated solution

1. Introduction

Membrane technology, as a state-of-the-art process, is going to be useful and practical in many industries. It has been used for the production of drinking water from seawater over the last 40 years [1], food and beverage industries for almost 25 years, and is gaining much interest in many other fields such as treatment of waste water, clarification and enrichment of processable products, dialysis, etc. [2,3].

Industrial salt always contain some amount of sulfate (SO_4^{2-}) and its accumulation in chlor-alkali brine leads to destruction of ion exchange membrane and precipitation of SO_4^{2-} on anode. It is worth noting that the major anionic impurity in the most brine systems is SO_4^{2-} [4]. Due to the recent development in the field of membrane technology, selective separation of SO_4^{2-} can be achieved using nanofiltration (NF) [5].

As mentioned in many scientific reports [6–8], owing to the higher ionic valence and bigger hydration radius, SO_4^{2-} can be partially separated from chloride (Cl^-) using NF process. This belongs to different phenomena and

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rejection mechanisms that happen through NF process such as Donnan phenomenon, dielectric exclusion, steric hindrance, electrostatic interactions, concentration polarization, and so forth [9–14].

With membrane electrolysis cells commonly used in chlor-alkali industries, there is specified about 7 g/L of Na_2SO_4 in the depleted brine. Therefore, many techniques such as purge of solution, ion exchange and precipitation have been applied to hold the SO_4^{2-} concentration below this level [4]. These conventional methods have major disadvantages such as environmental issues and lack of economic justification [4]. Accordingly, it is expected that the NF process as a promising technique can be an efficient tool with less environmental adverse side effects and better separation performance. There are many studies that focused on the applications dealing with solutions containing low SO_4^{2-} and Cl^- concentrations. Conversely, regarding the almost saturated chlor-alkali brine, limited information are available and there is a lack of fundamental knowledge for SO_4^{2-} removal from highly concentrated solution using NF process. Furthermore, the optimization of independent main parameters involving this process has not been reported so far.

Recently, Labban et al. [15] studied multi ionic interactions in water softening by means of NF hollow fiber membranes. Their results showed that the membrane could operate at low pressure, while maintaining relatively high rejection of multivalent ions. Also, they concluded that the membrane pore dielectric constant followed by the pore size were primarily responsible for the selectively high rejection of multivalent ions. In another report, Yan and coworkers [5] utilized a commercial Desal-DL NF membrane for the permeation of the single and binary salt solutions of NaCl and Na_2SO_4. They exhibited that by controlling the operational conditions, the membrane had a low rejection to Cl^- and a high rejection to SO_4^{2-} for single salt solutions. While using binary salt solutions, the membrane exhibited a bit higher rejection to SO_4^{2-} and much lower rejection to Cl^-. The reasons of these observations were related to permeate flow rate, Donnan equilibrium and specific area of the membrane. By following up the literature, it has been found many researchers have focused on the modeling of NF performance. For example, Geraldes and Alves [16] developed a computer program so-called Nano Filtran to simulate the mass transport of multi-ionic aqueous in charged NF membranes, based on the Donnan steric partitioning pore and dielectric exclusion (DSPM & DE) model. Their resulting model which is available under a free software license, has a good agreement with experimental and numerical data reported in the literature and also showed a great numerical stability. Afterward, a case study was carried out by Déon et al. [17] to develop a pore and polarization transport model (PPTM) for evaluating the operating conditions such as applied pressure, feed flow rate and divalent ion proportion. Interestingly, amid the rare studies on highly concentrated solutions NF process, Bargeman et al. [18,19] reported prominent results regarding the effect of membrane characteristics on separation performance during NF of practically saturated salt solutions. They showed that SO_4^{2-} retention was inversely related to pore radius, and also Cl^- retention was a function of SO_4^{2-} concentration difference between concentrate and permeate solutions.

Besides these above mentioned efforts, investigating the effects of operational parameters on permeate flow rate and retention of SO_4^{2-} and Cl^- has not been considered for highly saturated chlor-alkali brine. Therefore, a lack of knowledge has been yet remained pertained to correlations between operational parameters and transport phenomena in NF process of highly concentrated aqueous solutions. In this line, the highest and the lowest possible retention values of SO_4^{2-} and Cl^-, respectively, and also the highest possible permeate flow rate can be achieved by manipulating and optimizing the operational parameters. Eventually, these advantages can enhance the separation performance of NF membrane by using a series of design of experiment approaches i.e., Taguchi method.

Moreover, some commercialized SO_4^{2-} removal systems were also constructed. The Kvaerner Chemetics have developed a novel process for SO_4^{2-} removal from chlor-alkali brine based on NF process [20]. On the other hand, Chlorine Engineers Corp. Ltd., introduced a new desulfation system (NDS) using zirconium hydroxide, and also as an advancement of NDS technology, they have developed resin type new desulfation system (RNDS) containing zirconium hydroxide [21]. Although the trials carried out by them have provided data and understanding the role of parameters like temperature, pressure, pH, and feed concentration on retention, they have not illustrated transport phenomena mechanisms that play the indispensable roles on NF process.

The objective of this work is to investigate the effects of pH, temperature, pressure, feed flow rate and concentration of Na_2SO_4 and NaCl on permeate flow rate as well as the retention of SO_4^{2-} and Cl^- in NF process. Using Taguchi design, the effects of the above mentioned parameters on separation performance are evaluated. By means of analysis of variance (ANOVA), the contribution of each parameter on separation performance and reliability of the experimental data can be investigated. A qualitative study of almost saturated NF process is carried out by utilizing Taguchi design method and ANOVA, thereby discussing the phenomena and mechanisms of NF process. Chlorate (ClO_3^-) is another impurity in chlor-alkali brine like SO_4^{2-}, but with less harmful effects. Therefore, we also assessed the capability of NF process to separate ClO_3^- from brine.

2. Materials and methods

2.1. Materials and used commercial membrane

In all experiments, deionized water with a conductivity less than 10 µS/cm was used. All chemicals were supplied from Merck and were analytical reagent grades, used without further purification. The commercial NF membrane (NF-3) was supplied from Sepro. The composition of NF-3 membrane is a polyamide thin film composite membrane on a polyester backing with a polysulfone substrate. Table 1 summarizes the specification of NF-3 membrane product which reveals the variations of pressure, solute type and concentration against water flux and rejection of solute at 25°C and pH 7.5.

Table 1
The summary of NF-3 membrane product

Test pressure (psi/bar)	150/10.3	150/10.3
Solute concentration (mg/L)	2000	2000
Solute	$MgSO_4$	NaCl
Water flux (gfd*/Lmh**)	25/42	25/42
Solute rejection (%)	99	55

*gallon/ft^2/d **L/m^2/h

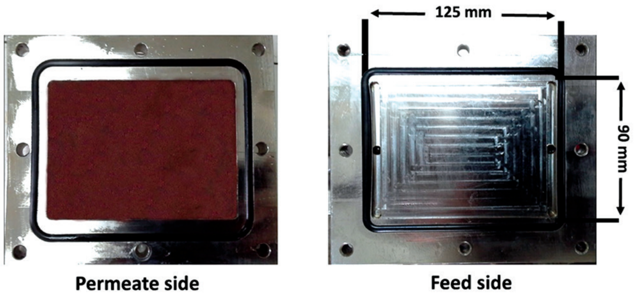

Fig. 2. The cross flow flat channel module.

2.2. Experiment setup and characterization

An overall schematic representation of the device used in this work is shown in Fig. 1. In order to keep the feed concentration constant, total recirculation of permeate and retentate were returned to the feed reservoir. Fig. 2 illustrates the cross flow flat channel module with specific area of 112 cm^2. As is seen from Fig. 1, the permeate chamber was maintained at atmospheric pressure. The NF membrane was placed inside the module which in turn its active layer facing downward. The feed flow channel was 1 mm in height and spacer was not used in this work.

For concentration measurements of SO_4^{2-} and Cl^-, ASTM D 516-07 and ASTM D 4458-94 were applied, respectively and also a modified colorimetric method was used for the detection of ClO_3^- based on the literature [22].

2.3. Filtration procedure

At first, NF membrane was immersed into deionized water for 24 h prior to use. To avoid membrane compression effect during the experiments, it was pressurized 9 bar for 45 min. Also, temperature, pressure and flow rates were controlled manually throughout the experiments. Since the parameters were adjusted in the predetermined values, the first sampling was taken after 45 min (stabilization time). Three samplings were done at time intervals of 5 min owing to ensure the steady-state process. If the average amount of two last samplings was approximately the same as the value of first sampling, the results are valuable to report. In the procedure of pH experiments, the pH setting took place with stabilization simultaneously.

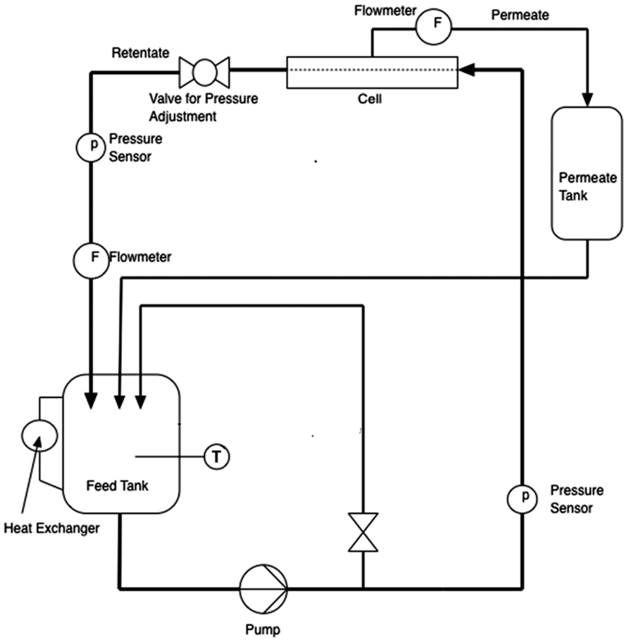

Fig. 1. An overall schematic representation of the device used in this work

2.4. Design of experiment and analysis of variance

To investigate and optimize the independent variables involved in the current work, Taguchi method was used. This approach is based on the statistical technique introduced by Fisher which studies simultaneously the effects of multiple variables on the responses. This method uses orthogonal arrays to reduce the number of experiments. Selection of a suitable orthogonal array depends on the number of factors and their levels [23,24].

Herein, the main factors were pressure, temperature, feed flow rate, and concentration of Na_2SO_4 and NaCl. Table 2 shows all factors along with their levels which provided an appropriate orthogonal array, L_{16}. Accordingly, 16 trials were designed and are represented in Table 3. In this table, the columns are orthogonal (Inner product of each column is equal to zero) and for each pair of columns, all combinations of factor levels occur.

Two main plots including S/N ratio and mean of means diagrams are extracted using Taguchi method that both of them analyze the effects of each factor on responses. The S/N ratio is the ratio of the means to the standard deviation (Noise), and hence three types of S/N ratio are defined as follows: the lower the better, the higher the better and the

Table 2
The values of main factors corresponding to their different levels

	Level			
Factor	1	2	3	4
NaCl concentration (g/L)	25	50	100	225
Na_2SO_4 concentration (g/L)	1	7	15	25
Temperature (°C)	27	45		
Pressure (bar)	5	9		
Feed flow rate (mL/min)	180	360		

Table 3
Taguchi L_{16} orthogonal array

Trial	NaCl concentration	Na_2SO_4 concentration	Temperature	Pressure	Feed flow rate
1	1	1	1	1	1
2	1	2	1	1	1
3	1	3	2	2	2
4	1	4	2	2	2
5	2	1	1	2	2
6	2	2	1	2	2
7	2	3	2	1	1
8	2	4	2	1	1
9	3	1	2	1	2
10	3	2	2	1	2
11	3	3	1	2	1
12	3	4	1	2	1
13	4	1	2	2	1
14	4	2	2	2	1
15	4	3	1	1	2
16	4	4	1	1	2

nominal the better. The S/N ratio with the higher the better characteristics is expressed in Eq. (1):

$$\frac{S}{N} = -10\frac{1}{n}\log\sum_{i=1}^{n}\frac{1}{Y_i^2} \tag{1}$$

where 'n' is the number of observations and 'Y_i' is the response factor (i.e., retention of SO_4^{2-} and Cl^- as well as permeate flow rate) on the i^{th} experiment. Also, the S/N ratio with the lower the better characteristic is defined based on Eq. (2):

$$\frac{S}{N} = -10\frac{1}{n}\log\sum_{i=1}^{n}Y_i^2 \tag{2}$$

In a multi factor design of experiment, Eq. (3) which is an individual linear model is used to investigate the effects of each factor on the responses:

$$Y_{i,j} = \mu + \tau_i + \beta_i + \ldots + \varepsilon_{i,j} \tag{3}$$

where 'μ' is the overall mean effects of factors on performance value; 'τ_i', 'β_i', etc., are the fixed effect of each factor in i^{th} level on performance value, and '$\varepsilon_{i,j}$' is the random error. '$\varepsilon_{i,j}$' is assumed to be normally distributed with zero mean. In this work, SO_4^{2-} retention and permeate flow rate results were considered as the higher the better and Cl^- retention results were considered as the lower the better.

The significance of each factor is determined using analysis of variance (ANOVA). To investigate the normality of the obtained experimental data before ANOVA, Shapiro test is utilized by R software [25]. It is worth noting that the normality of results is essential for ANOVA reliability.

F-ratio value at 95% confidence levels is used to determine the significant factors affecting the process.

Coefficient of determination, denoted R^2 is a measure that indicate how well data fit a statistical model. R^2 being closer to 1 indicates that the regression line better fits the data. The use of adjusted R^2 (R^2_{adj}) is an attempt to take into account the phenomenon of automatically and spuriously increase of R^2 when extra explanatory variables are added to the model. In this work, both R^2 and R^2_{adj} are represented.

At last, the impact of each factor is shown using the contribution percent which is defined as the ratio of sum of squares to total sum of squares. In the current work, this value has been also discussed.

2.5. Performance parameters

Performance parameters are usually defined in terms of rejection and permeate flux. Rejection is expressed in two ways of observed rejection and real rejection. Observed rejection (R) is calculated from the difference between the concentration of the solute in permeate and feed flow, according to Eq. (4):

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{4}$$

where 'C_P' is the permeate concentration and 'C_F' is the feed concentration. The real rejection (R_{real}) is calculated from the difference between the concentration of the solute in permeate flow and the concentration of the solute on the feed side membrane surface, according to the Eq. (5):

$$R_{real} = \left(1 - \frac{C_P}{C_M}\right) \times 100 \tag{5}$$

where 'C_M' is the concentration on the feed side membrane surface. In the case of experiments where concentration polarization has significant effect, this term gets more important.

Permeate flux is the result of a driving force acting on the feed solution. For a short term evaluation, without considering membrane fouling, permeate flux (j) can be described by the resistance model defined in Eq. (6) [13]:

$$j = \frac{\Delta P - \Delta\pi}{\eta\left(R_m + R_{CP}\right)} \tag{6}$$

where 'ΔP' is transmembrane pressure, '$\Delta\pi$' is osmotic pressure difference between bulk and permeate, 'η' is solvent viscosity, 'R_m' is intrinsic membrane resistance, and 'R_{CP}' is the resistance following concentration polarization layer. In industrial applications, fouling and cleaning procedures affect the permeate flux [2].

3. Five important mechanisms/phenomena

Most of NF membranes acquire electric charge when bring into contact with aqueous solution [26]. This electric charge generation is due to acid/base dissociation, counter ion site binding and competitive adsorption between anions and cations [9]. The transport mechanisms of ions through the membrane are ionic diffusion, electromigration and convection in the membrane pores. Equilibrium partitioning at the interface between the membrane and bulk solution is due to three separation mechanisms: steric hindrance, Donnan equilibrium and dielectric exclusion [7,14,16,26]. The difference between dielectric constant of the aqueous solution in the pores and dielectric constant of the bulk solution dominantly provides the rejection mechanism so-called dielectric exclusion [10]. Salting-out effect and concentration polarization which happen in highly concentrated solutions NF process are also important owing to almost saturated brine [19].

3.1. Charge formation

Charge of NF membranes is based on membrane material and the solution which is in contact with the membrane. As explained by Bandini [9], a polymeric NF membrane typically consist of hydrophobic functional groups (alkyl or aromatic chains) which alternate to hydrophilic functional groups ($-CONH_2$, $-COOH$, $-NH_2$, $-SO^-_3$, $-R_3N^+$, etc.). Therefore, the following charge formation mechanisms occur in NF process: (1) acid/base dissociation of hydrophilic functional groups, (2) competitive adsorption of cations and anions on hydrophobic sites, and (3) counter ion site binding on charged hydrophilic sites.

As the concentration of solution increases, the adsorption of charge on hydrophobic sites of membrane and screening of the dissociated hydrophilic sites increase owing to the site binding phenomenon [11]. Using highly concentrated solutions based on this current work, site binding phenomenon cause to almost screen all the dissociated hydrophilic sites and deactivate their contribution [11,13].

3.2. Dielectric exclusion

In NF process, the role of image forces and solvation energy difference between bulk and pores containing solution, determine the ions rejection mechanism based on the dielectric effect [10]. Image forces arise when an ion interacts with the boned electrical charges, induced by the ion, at the interface between materials with different dielectric constants [27] that in this work, they are brine and membrane. The magnitude of image force depends on the pore geometry, the ion valance, and the ratio of dielectric constants of the two media. For those membranes including strongly charged small pores, the screening of image forces is significant and the dielectric exclusion by the role of image force is negligible [14,27,28].

Bulk and pores containing solvent, have two different dielectric constants due to the distinct confinement and physico chemical environment. Smaller pores induce more significant orientation of water molecules, and hence the dielectric constant of solvent in pores is lower than the bulk solvent. An amount of energy is required to pass an ion from a solvent with a higher dielectric constant to a lower ones. This kind of dielectric exclusion is proposed by Bowen and Welfoot [29].

Déon et al. [30] showed that the physico chemical environment besides confinement play a key role on the value of dielectric constant. Their results revealed that the high charge density of divalent ion Ca^{2+} induced a more significant orientation of water molecules in its vicinity than monovalent ion Na^+ and thus led to a lower dielectric constant. Moreover, in the case of Desal DK membrane with average pore radius of 4.3×10^{-10} m (r_p), the dielectric constants of NaCl and $CaCl_2$ solutions were obtained 52 and 43, respectively. Also, strongly higher values of dielectric constants with the amounts of 79 and 68 were reported for NaCl and $CaCl_2$ solutions, respectively, while using Desal GH membrane with $r_p = 8.5 \times 10^{-10}$ m.

3.3. Concentration polarization

Transmembrane pressure as a driving force of NF process and selective transfer of some ion species through the membrane lead to increasing the concentration of non-permeating or slowly permeating components at the membrane/solution interface. The resulting concentrated layer at the membrane/solution interface reduces permeate flux through the membrane due to an increase in 'R_{CP}' based on Eq. (6). Concentration polarization also raises the permeation of rejected components, because of an increase in concentration gradient at both sides of the membrane.

Luo and Wan [13] divided concentration polarization phenomena into two categories: (1) the concentration polarization caused by convective transport and selective permeability that can be considered as "hydraulic induced concentration polarization". When such concentration polarization arises, the effective driving force would go down while observed rejection (R) may decline; (2) the concentration polarization caused by electrostatic adsorption; this kind of concentration polarization phenomenon was first proposed by Verliefde et al. [31] and can be considered as "charged induced concentration polarization". Due to the electrostatic adsorption, a large number of ions accumulate on/in membrane and thus the local ions concentration close to the charged groups, increases. By increasing charged induced concentration polarization, the real rejection (R_{real}) would be declined.

3.4. Donnan phenomenon

When a ternary system of non-permeating SO_4^{2-} ions and permeable Na^+ and Cl^- ions try to pass through the membrane, SO_4^{2-} remains in feed side but Na^+ and Cl^- transfer through the membrane. Therefore, an unbalanced distribution of charges on both sides of the membrane is occurred.

In NF process, Donnan exclusion is a subset of Donnan phenomenon and these two categories cannot be considered with the same interpretation. Frankly, the repulsion of co-ions from the charged NF membrane surface is described by Donnan exclusion. Consequently, the counter ions are also rejected owing to electroneutrality. On the other hand, regarding Donnan phenomenon, by adding Na_2SO_4, more amounts of Na^+ pass through the membrane, whereas SO_4^{2-} is not permeable; as a result more amounts of Cl^- have to pass through the membrane because of electroneutrality. This phenomenon decreases Cl^- retention and sometimes negative retention may even happen to form an equilibrium between two phases at both sides of the membrane and is defined as Donnan equilibrium. Accordingly, Donnan phenomenon is a general concept which covers the all above explanations.

3.5. Salting-out effect

Salting-out is a purification method that utilizes the reduced solubility of certain molecules in a solution of very high ionic strength, where the solubility of a specific salt is reduced by the addition of a common ion salt. In almost saturated brine similar to this current work, the salting-out effect can be occurred. In this way, increasing the concentration of Na_2SO_4 leads to salting-out of NaCl either by precipitation or transferring through the membrane. As the precipitation does not happen due to different reasons, salting-out effect causes NaCl traveling through the membrane [19].

4. Results and discussions

4.1. The results obtained from Taguchi method

Table 4 shows the three responses of SO_4^{2-} retention, Cl^- retention and permeate flow rate obtained from NF of the prepared chlor-alkali brine using Taguchi design methodology. All the experiments were done two times for increasing the precision and accuracy. The main objective of this work mentioned earlier were higher retention of SO_4^{2-}, higher permeate flow rate, and lower Cl^- retention.

Figs 3(a–e) to 5(a–e) depict the mean of means and S/N ratio diagrams of Taguchi method in which the effects of different parameters such as NaCl concentration, feed flow rate, pressure, Na_2SO_4 concentration, and temperature on those three responses were investigated.

4.2. ANOVA results and studies

With analysis of variance (ANOVA), the impact and significance of factors are determined by computing the F-ratio and the contribution percentage.

Regarding the normality of experimental data, Shapiro test results were 0.2927, 0.2471 and 0.2609 attributed to SO_4^{2-} retention, Cl^- retention and permeate flow rate, respectively. Considering the above values that all were higher than 0.05, it could be concluded that the results have normality for ANOVA analysis.

Table 4
Three responses of SO_4^{2-} retention, Cl^- retention and permeate flow rate based on the Taguchi L_{16} matrix

	SO_4^{2-} retention (%)		Cl^- retention (%)		Permeate flow rate (mL/min)	
Trial	1	2	1	2	1	2
1	88.01	88.11	42.4	44.0	1.02	0.95
2	91.00	92.10	37.6	40.8	0.96	0.81
3	89.17	88.70	36.3	36.8	2.44	2.20
4	89.03	89.10	26.7	27.7	1.89	1.59
5	89.10	90.80	43.0	45.6	2.41	2.31
6	91.14	92.09	41.8	39.8	1.97	1.88
7	88.90	90.27	39.4	36	0.98	1.10
8	89.20	89.00	37.6	36	0.59	0.72
9	86.40	87.21	44.0	41.8	1.42	1.31
10	90.90	91.37	38.6	36.6	1.08	0.90
11	91.40	92.42	40.0	37.3	1.39	1.19
12	91.50	92.80	33.3	34.6	1.06	0.93
13	87.30	86.30	30.0	29.7	1.90	1.71
14	90.60	90.40	29.1	28.9	1.65	1.48
15	93.20	93.20	30.5	32.4	0.38	0.30
16	93.40	93.20	29.2	32.4	0.24	0.25

The difference between R^2 (or R^2_{adj}) values and one is due to uncontrollable factors and interactions between the factors. The values of R^2 and R^2_{adj} for SO_4^{2-} and Cl^- retentions and permeate flow rate results were 0.9150 and 0.8800, 0.8931 and 0.8494, and 0.9722 and 0.9608, respectively.

ANOVA results of SO_4^{2-} retention are represented in Table 5. The p-value for pressure was 0.51942, so the pres-

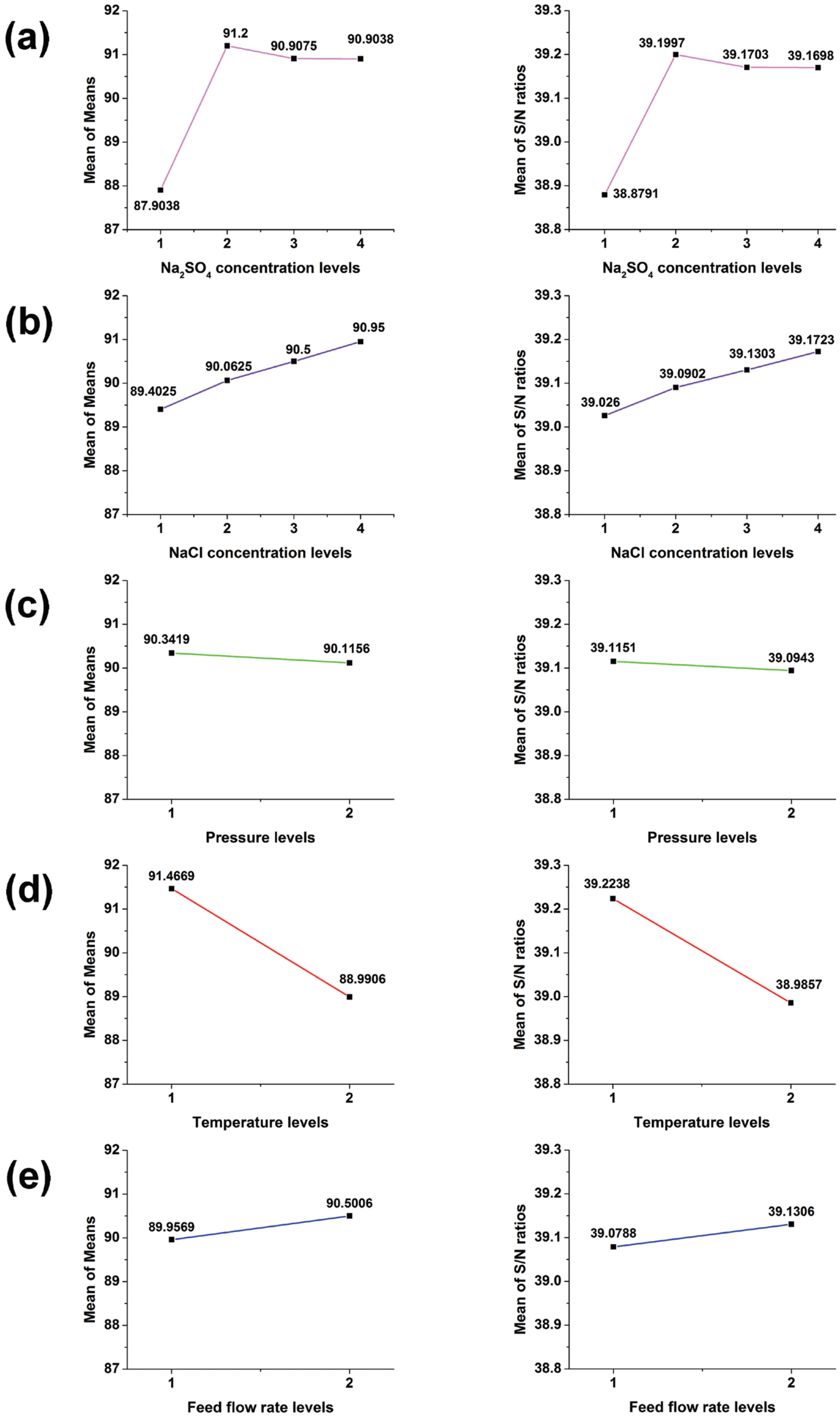

Fig. 3. Mean of means and S/N ratio diagrams of SO_4^{2-} retention: the effect of (a) Na_2SO_4 concentration, (b) NaCl concentration, (c) pressure, (d) temperature, and (e) feed flow rate.

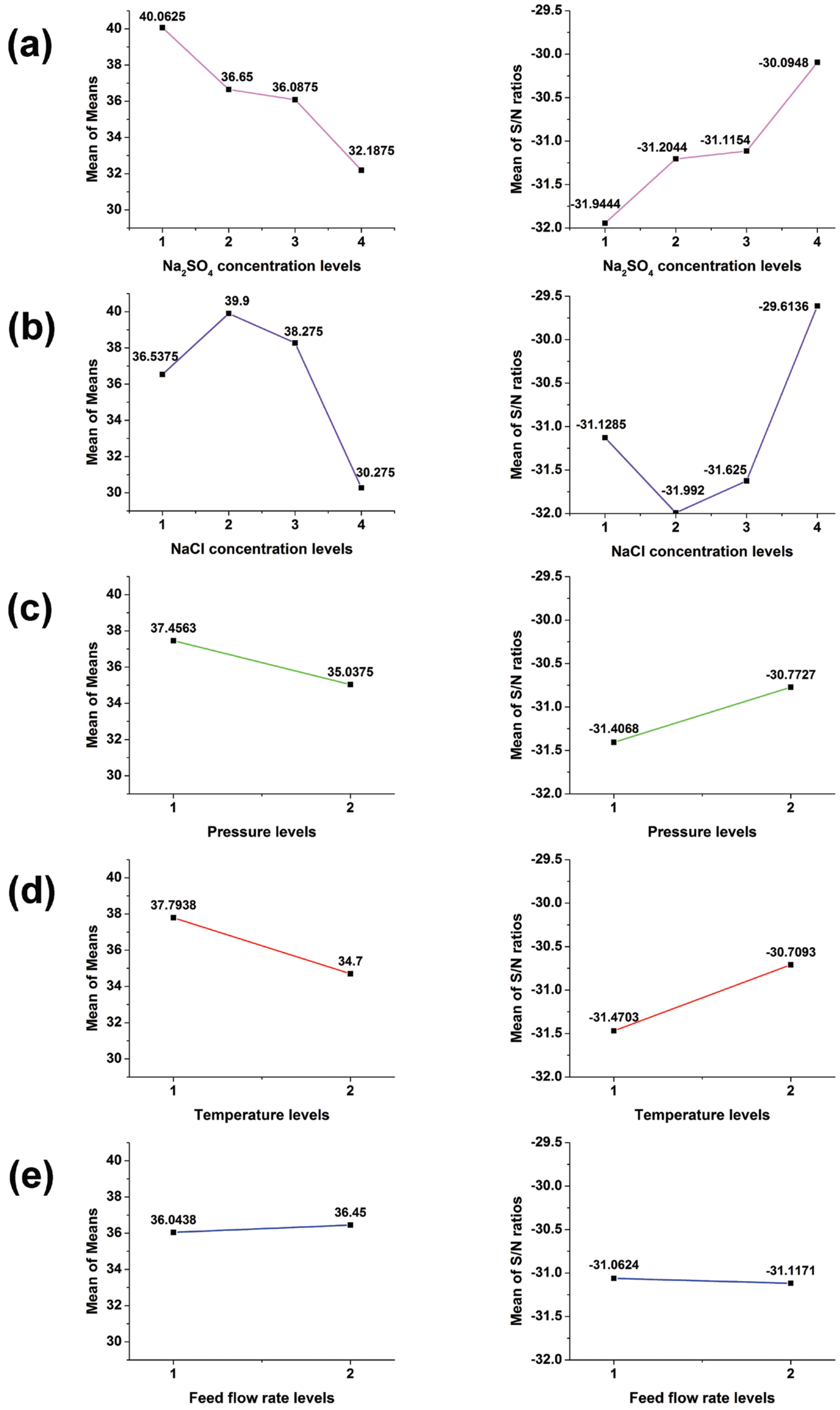

Fig. 4. Mean of means and S/N ratio diagrams of Cl$^-$ retention: the effect of (a) Na$_2$SO$_4$ concentration, (b) NaCl concentration, (c) pressure, (d) temperature, and (e) feed flow rate.

sure has no effect on SO$_4^{2-}$ retention. Based on the contribution percentage, the importance of each factor for SO$_4^{2-}$ retention was in the order Na$_2$SO$_4$ concentration, temperature, NaCl concentration and feed flow rate. Also, the contribution percentage diagram is shown in Fig. 6. As is seen, in the last column, the provided error was due to uncontrollable factors. In general, the error value should be less than 50% otherwise the results are not reliable [32].

ANOVA results attained from Cl$^-$ retention are represented in Table 6. As is observed, the feed flow rate has

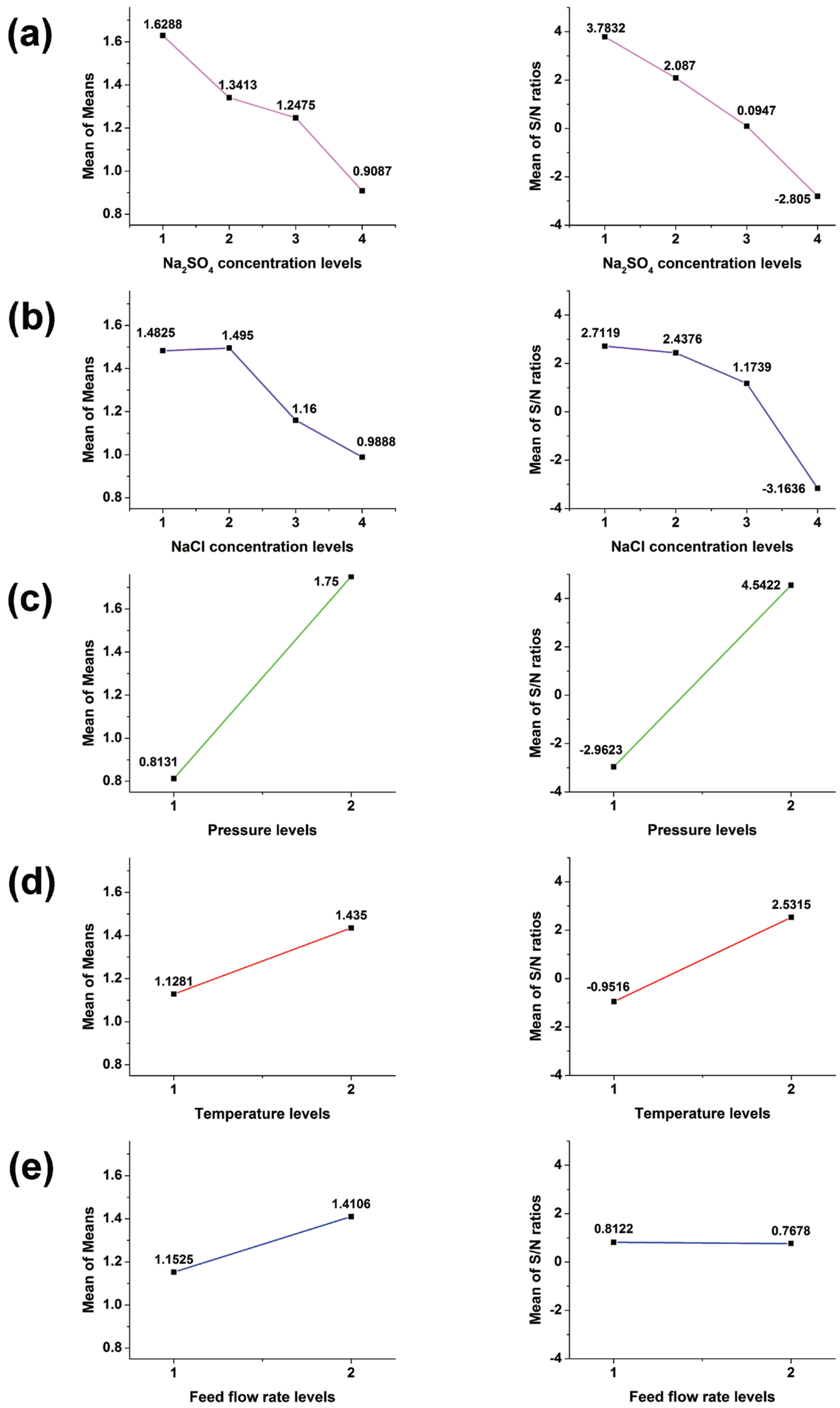

Fig. 5. Mean of means and S/N ratio diagrams of permeate flow rate: the effect of (a) Na_2SO_4 concentration, (b) NaCl concentration, (c) pressure, (d) temperature, and (e) feed flow rate.

no significant effect on Cl^- retention (p-value > 0.05) and the importance of each factor for Cl^- retention was in order NaCl concentration, Na_2SO_4 concentration, temperature and pressure. The contribution percent diagram is also exhibited in Fig. 7.

ANOVA results for permeate flow rate is also represented in Table 7. The p-value revealed that all factors have significant effect on the permeate flow rate. The contribution percent diagram is also depicted in Fig. 8. Finally, the descending order of factors in viewpoint of their influ-

Table 5
Analysis of variance (ANOVA) for SO_4^{2-} retention results

Factor	DF*	Sum Sq.	Mean Sq.	F-ratio	p-value (>F)	Contribution (%)
NaCl concentration	3	8.87	2.96	5.954	0.00393	6.867
Na_2SO_4 concentration	3	59.61	19.87	40.016	4.41e–09	46.149
Temperature	1	46.63	46.63	93.910	2.13e–09	36.099
Pressure	1	0.21	0.21	0.429	0.51942	0.162
F**	1	2.93	2.93	5.909	0.02367	2.268
Residuals	22	10.92	0.50	–	–	8.454

*Degree of freedom **Feed flow rate

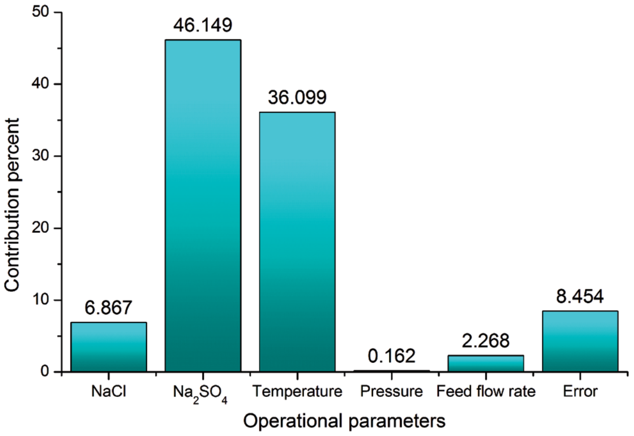

Fig. 6. The contribution percent diagram for SO_4^{2-} retention as a function of main factors using ANOVA.

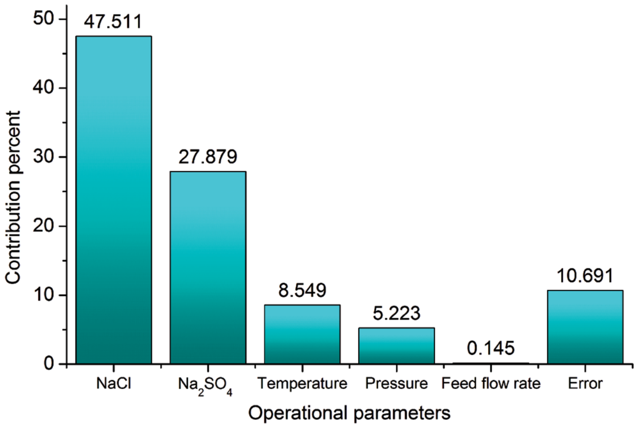

Fig. 7. The contribution percent diagram for Cl^- retention as a function of main factors using ANOVA.

ence on permeate flow rate was as follows: pressure, NaCl concentration, Na_2SO_4 concentration, feed flow rate and temperature.

4.3. Influence of operating conditions

4.3.1. Influence of Na_2SO_4 concentration

The impact of operational parameters on rejection has high sensitivity for solutes that are moderately rejected by the membrane and has low sensitivity for solutes that are highly rejected, and many researchers have observed this trend for SO_4^{2-} retention using NF membranes [2,5,7,33]. Accordingly, in the present work, SO_4^{2-} retention was between 86.3% and 93.4% that showed few considerable changes.

For highly concentrated solutions similar to this work, membrane separation performance is not a strong function of the membrane thickness and functional groups. In contrast, dielectric constant and average size of pores are

Table 6
Analysis of variance (ANOVA) for Cl^- retention results

Factor	DF*	Sum Sq.	Mean Sq.	F-ratio	p-value (>F)	Contribution (%)
NaCl concentration	3	425.7	141.88	32.599	2.83e–08	47.511
Na_2SO_4 concentration	3	249.8	83.27	19.132	2.47e–06	27.879
Temperature	1	76.6	76.57	17.593	0.000375	8.549
Pressure	1	46.8	46.80	10.753	0.003427	5.223
F**	1	1.3	1.32	0.303	0.587336	0.145
Residuals	22	95.8	4.35	–	–	10.691

*Degree of freedom **Feed flow rate

Table 7
Analysis of variance (ANOVA) for permeate flow rate results

Factor	DF*	Sum Sq.	Mean Sq.	F-ratio	p-value (>F)	Contribution (%)
NaCl concentration	3	2.516	0.839	49.48	6.02e–10	18.748
Na_2SO_4 concentration	3	2.342	0.781	46.06	1.19e–09	17.451
Temperature	1	0.300	0.300	17.72	0.000362	2.235
Pressure	1	6.055	6.055	357.20	4.33e–15	45.119
F**	1	1.834	1.834	108.17	5.88e–10	13.666
Residuals	22	0.373	0.017	–	–	2.779

*Degree of freedom **Feed flow rate

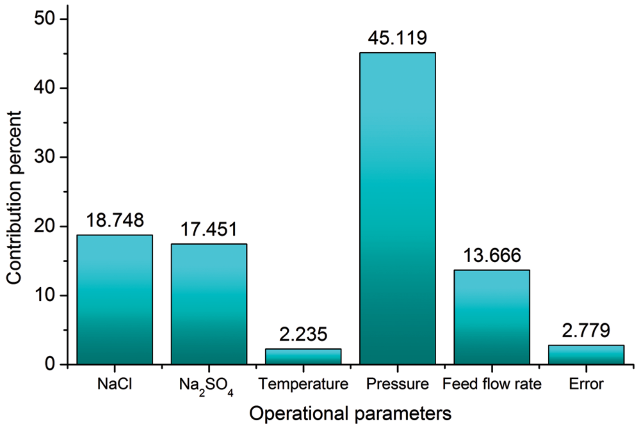

Fig. 8. The contribution percent diagram for permeate flow rate as a function of main factors using ANOVA.

two membrane properties which strongly affect NF performance [15].

As shown in Fig. 3a, SO_4^{2-} retention had no changes from level 2 to 4, but a different trend was occurred while decreasing this level from 2 to 1 in which a relative decrease in SO_4^{2-} retention was happened. It could be somehow changed the intermolecular interactions and properties of SO_4^{2-} since its concentration was totally lower than Cl^- at level 1.

From the results that are plotted in Fig. 4a, it is clear that by increasing Na_2SO_4 concentration, Cl^- retention was decreased. This could be related to three phenomena as follows:

(1) Donnan phenomenon: in highly concentrated solutions, all dissociated functional groups are screened, therefore Donnan exclusion effect is negligible. On the other hand, as the concentration of Na_2SO_4 increases, more Na^+ ions pass through the membrane compared to SO_4^{2-}. This behavior is due to the higher diffusion coefficient, lower hydration radius and ion valance of Na^+ than SO_4^{2-}. Therefore, electroneutrality of solutions at both sides of membrane causes higher Cl^- transfer through the membrane.

(2) Salting-out effect: concentration difference of SO_4^{2-} between retentate and permeate is the driving force for the salting-out of NaCl from the retentate to the permeate [10].

(3) Convective transport: increasing Na_2SO_4 concentration causes to decrease in permeate flow rate which reduces convective transport. As the convection effect decreases less water molecules pass through the membrane which lead to decrease in solute rejection.

Déon et al. [30] investigated the increase of Na_2SO_4 concentration led to an increase in concentration polarization; inversely, the addition of SO_4^{2-} played an opposite role on accumulation of Cl^- and resulted in the decrease of Cl^- concentration at membrane wall.

Permeate flow rate decreased as the concentration of Na_2SO_4 increased (Fig. 5a). The increase of SO_4^{2-} concentration has a great impact on concentration polarization followed by a decrease in permeate flow rate. Besides concentration polarization, an increase in characteristics such as viscosity, osmotic pressure difference and accumulation of ions was also occurred by increasing Na_2SO_4 concentration through the membrane pores; as a result, a decrease in permeate flow rate could be also observed.

Finally, based on ANOVA and Taguchi results, it could be concluded that the factor of Na_2SO_4 concentration was important parameter for Cl^- retention and permeate flow rate, especially SO_4^{2-} retention. As is seen from Fig. 3a, Na_2SO_4 concentration was suitable to be around 7 g/L. By considering Fig. 4a, it is evident that the increase of Na_2SO_4 concentration was appropriate, whereas it was inappropriate based on Fig. 5a for NF separation performance in this case. In consequence, this parameter should be optimized quantitatively.

4.3.2. Influence of NaCl concentration

It has been assumed that the effect of NaCl concentration on retention of SO_4^{2-} was due to the adsorption of Cl^- on membrane surface and inside pores, screening of dissociated functional groups by Na^+, and change in individual transport mechanisms of solute flux by increasing NaCl concentration.

Increasing adsorption of Cl^- onto the surface and inside pores of membrane due to the ascending NaCl concentration causes an increase in absolute volume charge density $|X_d|$ which results in an increase in retention of both SO_4^{2-} and Cl^-. Another important phenomenon for this observation refers to individual transport mechanisms of SO_4^{2-} flux. Pérez-González [8] reported that by increasing Cl^- to SO_4^{2-} ratio, contribution percent of diffusion was increased while it was decreased for convection and electromigration. In their study, the contribution of electromigration showed lower values for SO_4^{2-} than Cl^-, because SO_4^{2-} was a divalent ion, and hence the repulsion exerted by membrane was greater for SO_4^{2-} compared to Cl^- because of $|X_d|$.

Fig. 3b shows that by increasing NaCl concentration, retention of SO_4^{2-} was increased a little. This observation belonged to already screened functional groups at whole concentration ranges in this work, and also the increase of $|X_d|$ which led to lower contribution of electromigration.

The effect of NaCl concentration on rejection of Cl^- was pertained to four mechanisms including (1) concentration polarization, (2) Donnan phenomenon, (3) ratio of solute radius over the average pore ones, and (4) convection to diffusion ratio.

By increasing NaCl amount, the impact of concentration polarization was increased, ratio of solute radius over the average pore ones, and convection to diffusion ratio were decreased which all of them caused to decrease in Cl^- retention. In general, the ratio of the solute radius over the average pore ones decreases while increasing the ionic strength of the solution [18,19]. On the other hand, by increasing NaCl concentration, Donnan phenomenon impact on retention decreased due to the decline of SO_4^{2-} to Cl^- concentration ratio which led to an increase in Cl^- retention.

From the results of Cl^- retention that are plotted in Fig. 4b, it is obvious that as the concentration of NaCl was increased from level 1 to 2 and also from 2 to 4, Cl^- retention showed an increase and then decrease, respectively. The increase trend was due to the decrease of Donnan phenomenon impact and the decrease trend was related to three reasons including the increase of concentration polarization and the decrease of solute radius to average pore ratio as well as convection to diffusion ratio.

As is shown in Fig. 5b, increasing the concentration of NaCl led to a decrease in permeate flow rate. This trend was due to increasing concentration polarization, viscosity, osmotic pressure difference, and accumulation of ions through the membrane. As it can be seen from Fig. 8, the amount of contribution percent was the same approximately for NaCl and Na_2SO_4 concentrations (~18%). By considering the concentrations of NaCl and Na_2SO_4 solutions in the range of 25–225 g/L and 1–25 g/L, respectively, it could be concluded that Na_2SO_4 concentration variations have higher impact.

Eventually, based on ANOVA and Taguchi results, NaCl concentration has a high impact on permeate flow rate and Cl^- retention. Also, this parameter has a moderate effect on SO_4^{2-} retention. As is seen from Fig. 4b, low and high concentrations of NaCl were suitable for minimizing Cl^- retention. Also, Fig. 3b shows that the increase of NaCl concentration could have advantage for better performance of this separation, whereas it was inappropriate based on Fig. 5b for NF separation performance. In consequence, this parameter should be optimized quantitatively.

4.3.3. Influence of pressure

The solute flux through the membrane (J_s) can be expressed by Eq. (7) [5,34]:

$$J_s = -\left(p\Delta x\right)\frac{dC}{dx} + \left(1-\sigma\right)J_v C \tag{7}$$

where 'J_v' is the volumetric flux, 'σ' and 'p' are reflection coefficient and solute permeability, 'Δx' is the membrane thickness and 'C' is the concentration of solute. According to this equation, the solute flux through the membrane is due to the diffusion and convection mechanisms caused by the concentration and hydraulic pressure differences, respectively. Therefore, the influence of pressure on retention is investigated by concentration polarization and dilution effects. As the pressure increases, the convection transport effect is increased followed by more water molecules pass through the membrane which lead to increasing the solute rejection. This phenomenon is known as "dilution effect". In parallel, by increasing the pressure, the concentration polarization is increased, resulting a decrease in solute rejection.

Many authors have observed an increase in the solute rejection by raising the pressure owing to the dilution effect [2,5,7,15]. A new definition of rejection that is called "limiting rejection" is also reported by some researchers as follows [15,35]:

$$R_{lim} = 1 - K_{i,c}\phi_i \tag{8}$$

$$\phi_i = \left(1-\lambda_i\right)^2 \tag{9}$$

where 'λ_i' is the ratio of solute Stokes radius to effective pore radius, '$K_{i,c}$' is the convection hindrance factor, and 'ϕ_i' is steric partitioning coefficient.

Limiting rejection emphasizes that over a certain value for rejection, increasing the permeate flux does not lead to increasing rejection, which means any increase in convective transport beyond this point is offset by increasing concentration polarization [15,35].

Déon et al. [17] concluded that the applied pressure did not change the thickness of concentration polarization layer. Interestingly, they revealed that the pressure has a notable impact on the ion accumulation at the membrane wall, and hence it strongly reinforced the concentration polarization phenomenon.

In a few studies, it has been observed a little decrease in solute retention by increasing pressure for ions [2] and glucose [18]. Furthermore, Luo and Wan [13] discussed both dilution and concentration polarization effects simultaneously and concluded that in overall, on the one hand, the dilution effect increases the real rejection and on the other hand, the concentration polarization decreases the observed rejection.

As is shown in Figs. 3c and 4c, by increasing pressure from 5 to 9 bar, SO_4^{2-} retention did not change, whereas Cl^- retention was decreased a little. This trend of Cl^- retention could be due to higher impact of concentration polarization than dilution effect which might be occurred because of high concentration of NaCl.

Volumetric flux (J_v) can also be expressed as follows [5,34]:

$$J_v = L_p\left(\Delta p - \sigma\Delta\pi\right) \tag{10}$$

where 'L_p' is pure water permeability, 'Δp' and '$\Delta\pi$' are hydraulic pressure and osmotic pressure differences. As expressed in this equation, pressure is the driving force of NF process and its increase leads to the raise of permeate flow rate. This behavior can be seen from Fig. 5c.

Finally, based on ANOVA and Taguchi results, it could be concluded that the pressure was the most important parameter for varying the permeate flow rate. On the other hand, this factor showed a negligible influence on the variation of Cl^- and SO_4^{2-} retentions. Consequently, the increase of pressure is useful to improve the performance of NF separation process in chlor-alkali industries, qualitatively.

4.3.4. Influence of temperature

In two studies related to the effect of feed temperature on permeation characteristics and pore size of NF membranes, both Sharma et al. [36], and Dang et al. [37] suggested that the average pore radius was increased while raising feed temperature.

The effect of temperature on NF process was divided into two categories: (1) increase of diffusion rate and decrease of viscosity by raising temperature, which is called "direct effect" and (2) swelling the polymer-based membrane by increasing temperature, which is called "indirect effect" [13].

As is shown in Figs. 3(d) and 4(d), it is obvious that by increasing temperature both SO_4^{2-} and Cl^- retentions were decreased due to both direct and indirect effects.

Increase of permeate flow rate owing to increasing temperature is also obvious from Fig. 5d that also related to two phenomena above mentioned. Similarly, some literature also reported these observations and discussions [37,38].

In chlor-alkali industries, based on NF operating temperature, a system of heat exchanger may be necessary, due to the high temperature (~80°C) of depleted brine. Therefore, temperature should be optimized for each chlor-alkali industry based on financial point of view.

Finally, based on ANOVA and Taguchi results, it could be concluded that the temperature has a significant effect on SO_4^{2-} and Cl^- retentions. It also has a minor effect on permeate flow rate. On one hand, the increase of this factor showed advantages for permeate flow rate and Cl^- retention, on the other hand, it was unsuitable for SO_4^{2-} retention. The selection of optimized temperature depends on many qualitative and quantitative financial and operational aspects of chlor-alkali industries.

4.3.5. Influence of feed flow rate

Feed flow rate affects concentration polarization layer. By increasing feed flow rate, a reduction in thickness of concentration polarization layer is happened, leading to a decrease in solute accumulation at membrane wall [17].

As is shown in Figs. 3e and 4e, by increasing feed flow rate from 180 to 360 mL/min, SO_4^{2-} retention was increased a little, whereas Cl^- retention had no changes. SO_4^{2-} retention trend was owing to the concentration polarization attenuation. In fact, the concentration polarization layer not only contains the viscose sublayer but it can also involve in the buffer layer [17]. As the feed flow rate increases, turbulence is increased followed by increasing diffusion between concentration polarization layer and bulk solution. Therefore, the effect of concentration polarization on NF process is declined. On the other hand, there was no change in Cl^- retention by varying feed flow rate owing to high concentration of NaCl.

S/N ratio diagram shows that feed flow rate has no influence on permeate flow rate [Fig. 5(e)], whereas mean of means diagram exhibits that the increase of feed flow rate led to an increase in permeate flow rate. This kind of contradiction sometimes happens between S/N ratios and mean of means diagrams. Clearly, the concentration polarization attenuation was occurred by increasing feed flow rate, would cause to increase the permeate flow rate. Therefore, the mean of means diagram has been considered owing to showing the right influence of feed flow rate on permeate flow rate.

Yunoki et al. [39] investigated the cross flow velocity effect on filtration performance of NaCl and mono sodium glutamate solution. The rejection of Cl^- was increased by raising the cross flow velocity when the Cl^- rejection was positive. Whereas, Cl^- rejection was decreased by increasing the cross flow velocity when the rejection of Cl^- was negative. Positive and negative Cl^- rejections were attributed to increasing and decreasing Cl^- concentration towards the membrane surface, respectively.

Finally, based on ANOVA and Taguchi results, it could be concluded that the feed flow rate has significant influence, minor impact and no effect on permeate flow rate, SO_4^{2-} retention, and Cl^- retention, respectively. From industrial point of view, an increase in feed flow rate causes higher pressure drop, which is a function of module geometry, type of spacer and cross flow velocity. Increasing the feed flow rate could improve the performance of NF membrane in this work; however, this issue requires more operating and capital costs.

4.3.6. Influence of pH

The effect of pH on retention and permeation in NF process is a complicated behavior due to changes in membrane-solution and solution-solution interactions. The zeta potential of membranes associated with acidic functional groups becomes more negative as pH increases. With the same approach, membranes with basic functional groups are positively charged in a wide range of pH values. Membranes without ionic groups relatively show amphoteric behavior; i.e. negatively and positively charged at high and low pH, respectively [2]. This could be ascribed to the adsorption of ions from solution, which may involve OH^- or Cl^- and H^+ or K^+ species. Literature reviews have demonstrated that salt retention is influenced by pH due to the variation in membrane charge density through the dissociation of functional groups and adsorption of ions on the membrane surface and pores. Addition of acid or base to set pH in a membrane system leads to changes in permeability, zeta potential, and concentration polarization.

Herein, pH experiments were conducted in the pH range of 5–10 by the stepwise addition of concentrated NaOH solution to the feed reservoir. The operating conditions were as follows: pressure 9 bar, temperature 27°C, and feed flow rate 180 mL/min.

As is obvious from Figs. 9a, b, by increasing pH, Cl^- retention has increased while SO_4^{2-} retention was kept constant. It has been reported that pH value is an impressive factor for Cl^- retention but no clear correlation between Cl^- retention and pH value has been reported [2,40]. At the present work, it could be concluded that the increase of Cl^- retention by increasing pH was owing to higher amount of H^+ and OH^- permeations than that of Na^+ and Cl^- ions, respectively. This observation was owing to higher ionic mobility and lower size of H^+ and OH^-. In Regards to electroneutrality, the increase of pH from 7 to 10 leads to higher permeation of OH^-, and consequently lower permeation of Cl^-. On the other hand, by decreasing pH from 7 to 5, higher amount of H^+, consequently lower Na^+ (or higher Cl^-) pass through the membrane, which results in the decrease of Cl^- retention. Fig. 9b also shows that higher concentration reduces the influence of pH on retention.

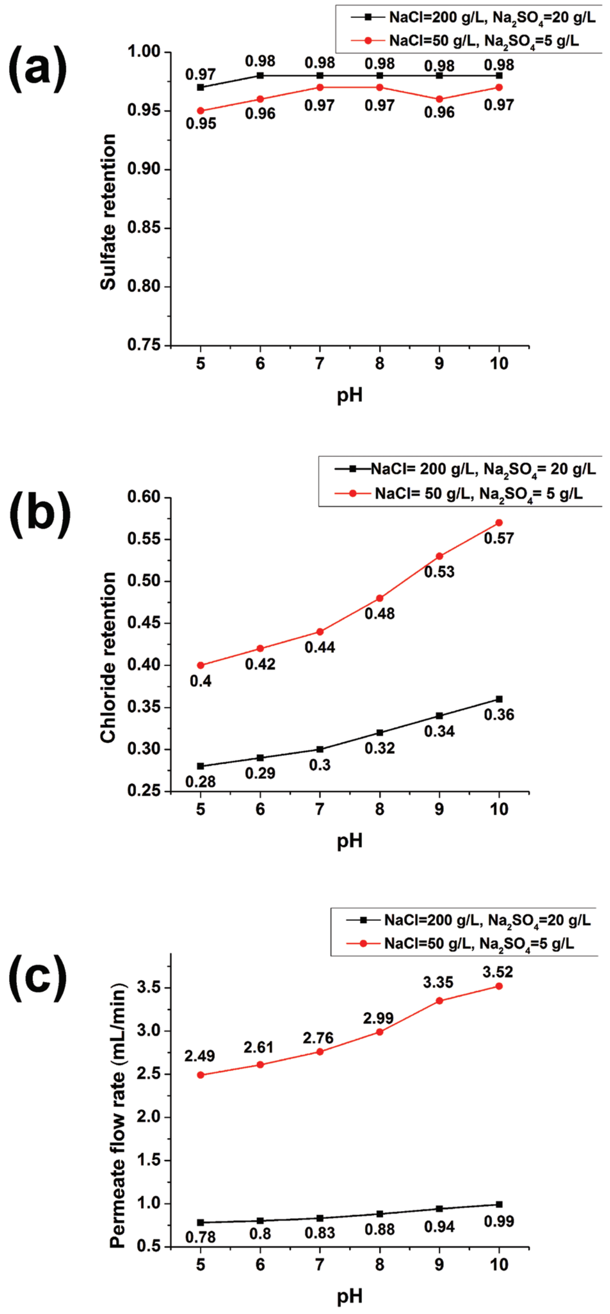

Fig. 9. Influence of pH variations on (a) SO_4^{2-} retention, (b) Cl^- retention, and (c) permeate flow rate.

Generally, an increase in pH leads to increase the membrane hydrophilicity property. It is shown in Fig. 9c that the permeate flow rate was increased by increasing pH, and found weaker dependency on pH at higher concentrations.

4.4. Chlorate retention

Depleted brine in chlor-alkali industries will be physically saturated with chlorine; and some chlorine will react to form hypochlorite. Some of the hypochlorite molecules that form in the anolyte will react to form ClO_3^- [4]. This ion concentration keeps rising in the brine circuit and has to be removed along with the SO_4^{2-}. At the present work, the separation of ClO_3^- from brine using NF was also investigated. In order to study the separation performance of ClO_3^-, salt concentrations were set as follows: NaCl 100 g/L, Na_2SO_4 7 g/L, and $NaClO_3$ 10–100 g/L. As is obvious from Fig. 10, ClO_3^- retention was much lower than SO_4^{2-} retention because of lower ionic valance of ClO_3^-. The ClO_3^- retention slightly decreased as its concentration increased because of (1) concentration polarization phenomenon and (2) decrease of convection to diffusion rate ratio as a result of decrease in permeate flow rate. It could be concluded that NF process was more suitable for the separation of SO_4^{2-} from brine than ClO_3^-.

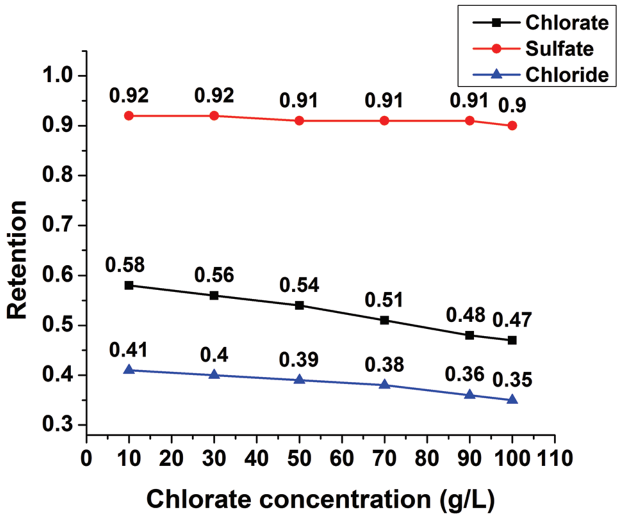

Fig. 10. Comparison of ClO_3^-, SO_4^{2-} and Cl^- retentions using NF process.

5. Conclusions

We successfully carried out the NF process using NF-3 (Sepro) membrane for SO_4^{2-} removal from highly concentrated chlor-alkali brine prepared in house. According to the experimental results, SO_4^{2-} and Cl^- retentions, and permeate flow rate were ranged between 86.3–93.4%, 26.7–45.6% and 0.24–2.44 mL/min, respectively for the flat sheet membrane with specific area of 112 cm^2 at predetermined conditions. The pressure impacts were attributed to the concentration polarization and dilution effects. The obtained results showed that the pressure had no effect on SO_4^{2-} retention; however Cl^- retention decreased a little by increasing the pressure. On the other hand, as it was expected, the permeate flow rate was increased by increasing the pressure. Temperature effects were investigated by direct and indirect effects. These effects led to decrease the SO_4^{2-} and Cl^- retentions as well as increase the permeate flow rate by increasing the temperature. An increase in feed flow rate resulted in attenuation of concentration polarization layer and had advantages for SO_4^{2-} retention and permeate flow rate. Moreover, it had no effect on Cl^- retention. The concentrations of NaCl and Na_2SO_4 had great effects on retentions of SO_4^{2-} and Cl^- as well as permeate flow rate. The increase of Na_2SO_4 concentration caused to decrease Cl^- retention due to the Donnan phenomenon, salting-out effect, and reducing convective transport. In the case of SO_4^{2-} retention, the best Na_2SO_4 concentration was around 7 g/L, because a burst reduction in SO_4^{2-} retention was occurred at lower concentration of Na_2SO_4. The increase of NaCl concentration led to a little increase in SO_4^{2-} retention due to raising the absolute membrane charge density, resulting electromigration decline. Increasing the Cl^- retention by raising NaCl concentration was owing to Donnan phenomenon, and thereafter its decrease was related to the decline of solute radius to average pore radius ratio, reducing convective transport, and increase in concentration polarization effect. The increase of NaCl and Na_2SO_4 concentrations resulted in a decrease in permeate flow rate with more influence of Na_2SO_4 than NaCl concentrations. Afterward, it was showed that pH value is important for the Cl^- retention and permeate flow rate, and it had almost no influence on SO_4^{2-} retention. Increasing pH value caused a raise in Cl^- retention and permeate flow rate. Finally, ClO_3^- retention from brine, using NF process, was also investigated separately and it was concluded that this process was not suitable for ClO_3^- retention compared to SO_4^{2-} retention.

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Symbols

S/N — Signal to noise ratio
n — Number of observations
Y — Response factor
μ — Overall mean effects of factors on performance value
τ — Fixed effect on each factor
β — Fixed effect on each factor
ε — Random error
C_P — Permeate concentration (mol/m^3)
C_F — Feed concentration (mol/m^3)
R_{real} — Real rejection
R — Observed rejection
C_M — Concentration on the feed side membrane surface (mol/m^3)
ΔP — Transmembrane pressure (Pa)
$\Delta\pi$ — Osmotic pressure difference between bulk and permeate (Pa)
η — Solvent viscosity (kg/m s)
R_m — Intrinsic membrane resistance (1/m)
R_{CP} — Resistance following concentration polarization layer (1/m)
j — Permeate flux (m^3/m^2 s)
J_s — Solute flux (mol/m^2 s)
J_v — Volumetric flux (m^3/m^2 s)
σ — Reflection coefficient
p — Solute permeability (m/s)
Δx — Membrane thickness (m)
λ — Ratio of solute Stokes radius to effective pore radius
$K_{i,c}$ — Convection hindrance factor
L_p — Pure water permeability (s m^2/kg)
R_{lim} — Limiting rejection
ϕ_i — Steric partitioning coefficient
r_p — Pore radius (m)
X_d — Volume charge density (mol/m^3)
R^2 — Coefficient of determination
R^2_{adj} — Adjusted coefficient of determination
ANOVA — Analysis of Variance
NF — Nanofiltration
p-value — Probability value
F-ratio — Fisher ratio
DF — Degree of freedom

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