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Influence of operating conditions on the retention of nickel in water by nanofiltration

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ABSTRACT

Discharge of heavy metals from metal processing industries is known to have adverse effects on the environment, high toxicity and tendency to accumulate in living organisms. Conventional treatment technologies (chemical precipitation, chemical oxidation or reduction, ion exchange…) for removal of heavy metals from aqueous solution are not economical and generate huge quantity of toxic chemical sludge. Against this pollution, very strict standards were imposed for heavy metal content in water because of their high toxicity. The objective of this study was to investigate the retention heavy metals by nanofiltration. The first part of this study deals with the characterisation of the different types of nanofiltration membranes used (HL, NF200). In the second part the effects of feed pressure, ionic strength, concentration and pH on the retention of nickel ion were investigated. Results show that the rejection values changed according to the type of the NF membrane used. In addition, the experimental data were analysed using the Spiegler–Kedem model and the transport parameters, i.e., the reflection coefficient (σ) and solute permeability (P_s) have been determined.

Keywords: Nanofiltration; Nickel; Wastewater; Spiegler–Kedem model

1. Introduction

Increased use of metals and chemicals in process industries (such as mining, metallurgical, electronic, electroplating and metal finishing…) has resulted in generation of large quantities of effluent that contain high level of toxic heavy metal ions and their presence poses environmental problems due to their nondegradable. Furthermore, most of the metal ions are toxic to the human body and living organisms. Against this increased pollution, very strict standards were imposed for heavy metal content in water. Precipitation, ion exchange, solvent extraction, electrochemical treatment, chemical oxidation or reduction, and adsorption onto activated carbon are the conventional methods for removal of heavy metal ions from aqueous solutions [1]. However conventional treatment technologies are not economical and generate huge quantity of toxic chemical sludge.

In the recent years nanofiltration (NF), one of the promising membrane processes, has been used for the removal of dissolved organic (dyes, pesticides, etc.) and inorganic contaminants (nitrate, arsenate, and heavy metal) from water and industrial effluents [2–5]. The advantages of NF over the classical techniques are the selective separation of ions and continuous operation without the need for frequent regeneration, coupled with a low-chemical impact and modest energy demand. Nanofiltration is a pressure driven process lying between ultrafiltration and reverse osmosis. NF membranes have smaller pore size (≈1 nm) and low molecular weight cut-offs (200–1000 g/mol). They also have a surface electrostatic charge which gives them great selectivity towards ions or charged molecules. Thus, the separation of ions using NF membranes is mainly based on a combination of size and charge effects. Additional phenomena, can also affect membrane performance, i.e., specific adsorption, dielectric phenomena and transport effects.

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The objective of the research described here was to investigate the retention of nickel from aqueous solutions by different nanofiltration membranes. The efficiency of nanofiltration was shown as a function of some experimental parameters (pressure, ionic strength, pH). The Spiegler–Kedem model was used to calculate the phenomenological parameters, i.e., the reflection coefficient (σ) and the permeate permeability (P_s).

2. Materials and methods

2.1. The nanofiltration membrane and chemicals

Two commercial polymeric membranes with different MWCO values were used in this study, NF200 and Desal-HL. An overview of the membrane properties, as indicated by the manufacturers, is given in Table 1.

Prior to experiments each membrane was soaked in water for 24 h in order to eliminate conservation products. The membrane was subjected to compaction for 3 h at an operating pressure of 20 bar and a temperature of 25°C, then pure water permeability was determined.

Sodium salts NaCl, $NaNO_3$, Na_2SO_4, $MgCl_2.6H_2O$ and $MgSO_4$ were provided from Fluka, $NiCl_2.6H_2O$ from May. Baker were used as received. NaOH and HCl were used to adjust the pH of feed solutions. CAS numbers for chemicals are given in Table 2.

All electrolyte solutions were prepared with ultrapure water produced by Milli-Q Gradient unit (Millipore).

2.2. Procedure

The permeations were conducted using a laboratory scale membrane unit P-28 from CM-Celfa (Switzerland). The unit comprises the membrane cell with integrated feed tank, pump, pressure indicator, pressure relief and safety valve. The membrane with effective filtration area of 28 cm^2 was supported by the porous stainless steel disc. A schematic diagram of the apparatus is shown in Fig. 1. Each experiment consists of a permeation of a 500 mL of solute at a fixed pressure (P = 3, 5, 7, 9 and 11 bar).The permeate was not recycled in the feed tank and no more than 30mL was collected in any experiment. The effect of this volume on the variation of the concentration of the feed was neglected. The temperature of the circulating feed was maintained at 25°C by a thermostat bath and the cross flow velocity was 2 ms^{-1}. The pressure was varied between 3 and 11 bar using pressurised nitrogen gas as a driving force. Following each experiment, the circuit was cleaned with ultrapure water at 5 bar for 30 min. This procedure was followed by nanofiltration of ultrapure water to ensure that the initial membrane pure water permeability was restored. For a given pressure, the feed solution was circulated until the whole system reached the steady state. The permeate flux was then determined by measuring the time corresponding to 25 mL permeate volume. In this study, high cross flow was adopted for all experiments to eliminate the concentration polarization effect. Thus, the membrane retention R is approximately equal to observed retention, and is defined as:

Table 1
Overview of commercial flat sheet nanofiltration membranes used in experiments.

Membrane	Desal HL	NF200
Manufacturer	Osmonics	Filmtec/Dow
Composition	polyamide	poly (piperazine amide)
MWCO*	150–300	200–300
Pore radius (nm)	0.48 [2]	0.5[a]
Permeability (L/m^2.h.bar)[a]	10.88[a]	10.01[a]
Maximum temperature (°C)	50	40
Maximum pressure (bar)	40	41
pH range	1–11	3–10

*MWCO: molecular weight cut off; as indicated by the membrane manufacturer (reference value).

[a] Own measurements [6].

Table 2
CAS numbers for chemicals used.

Solute	Sodium chloride	Sodium nitrate	Sodium sulfate	Magnesium chloride hexahydrate	Magnesium sulfate	Nickel chloride hexahydrate	Sodium hydroxide	Hydrogen chloride
CAS number	7647-14-5	7631-99-4	7757-82-6	7791-18-6	7487-88-9	7791-20-0	1310-73-2	7647-01-0

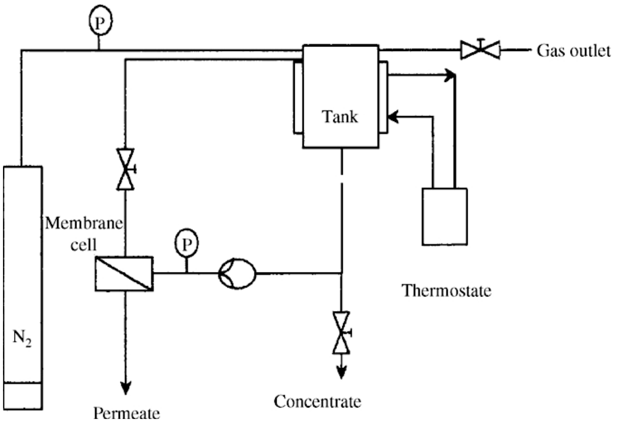


Fig. 1. Schematic of the experimental nanofiltration system.

$$R = 1 - \frac{C_p}{C_f} \tag{1}$$

where C_p and C_f are permeate and feed concentrations respectively.

Permeate flux J_v ($L.h^{-1}.m^{-2}$) was calculated as follow:

$$J_v = \frac{V}{\Delta t.S} \tag{2}$$

where V (L)is the volume of permeate collected within time Δt *(h)* and S is the membrane area (m^2).

2.3. Analytical methods

Concentration of inorganic salts NaCl, $MgCl_2$ and Na_2SO_4 were measured by conductivity in single solute systems and by atomic absorption spectrophotometry (analytiKjna AAS Vario 6) in the mixture systems. The concentrations of Nickel were measured by atomic absorption spectrophotometry (analytiKjna AAS Vario 6). The pH was measured by an ionometer Consort C832.

2.4. Transport equations

The transport of the solute through NF membranes can be described by irreversible thermodynamics where the membrane is considered as a black box. Kedem and Katchalsky [7] proposed the relation of the volume flux J_v and the solute flux J_s through a membrane in the following equations:

$$J_v = L_p(\Delta P - \sigma \Delta \pi) \tag{3}$$

$$J_s = P_s \Delta C + (1-\sigma) C J_v \tag{4}$$

C is the solute concentration in the feed solution, ΔC is the concentration difference of solute across the membrane, ΔP and $\Delta \pi$ is respectively the pressure difference and the osmotic pressure difference across the membrane.

The fluxes J_v and J_s are related to three membrane parameters σ, P_s and L_p, reflection coefficient, solute permeability and pure water permeability, respectively. As can be seen in Eq. (4) the solute flux is the sum of diffusive and convective terms. Solute transport by convection takes place because of an applied pressure gradient across the membrane. A concentration difference on both sides of the membrane causes diffusive transport. Spiegler and Kedem [8] used the above equations and obtained the expression of the rejection rate of the solute related to hydrodynamic flux:

$$R_{obs} = \frac{\sigma(1-F)}{1-\sigma F} \tag{5}$$

$$F = \exp\left[-\frac{(1-\sigma)J_v}{P_s}\right] \tag{6}$$

where R_{obs} is the observed rejection and J_v the water flux.

The reflection coefficient, σ, corresponds to maximum solute rejection, achieved only at infinite pressure differential (pure convection), and solute permeability, P_s, corresponds to purely diffusive transport when $J_v \to 0$. The parameters σ and P_s can be determined from the experimental data of rejection (R) as a function of water flux (J_v) using the best-fit method.

The solute permeability coefficient P_s is a function of the diffusivity (D_s) and the distribution coefficient (K_s) as given by equation 7 [9]:

$$P_s = \frac{D_s.K_s}{\Delta x} \tag{7}$$

On the other hand, the Spiegler-Kedem model is not able to predict accurately the solute rejection at very low permeate flux, whatever the membrane nature and solute concentration [10]. According to Eqs. (5 and 6), the retention converge to zero when the permeate flux is zero. This model is only usable in the higher range of permeate flux.

3. Results and discussion

3.1. Salt retention measurements

Before conducting the nickel retention experiments, a serie of ion rejection tests was performed to understand the mechanisms governing ion retention by membranes. Three salts were chosen to span a variety electrolyte types including symmetric 1–1 electrolyte (NaCl) as well as asymmetric 2–1 and 1-2 electrolytes ($MgCl_2$ and

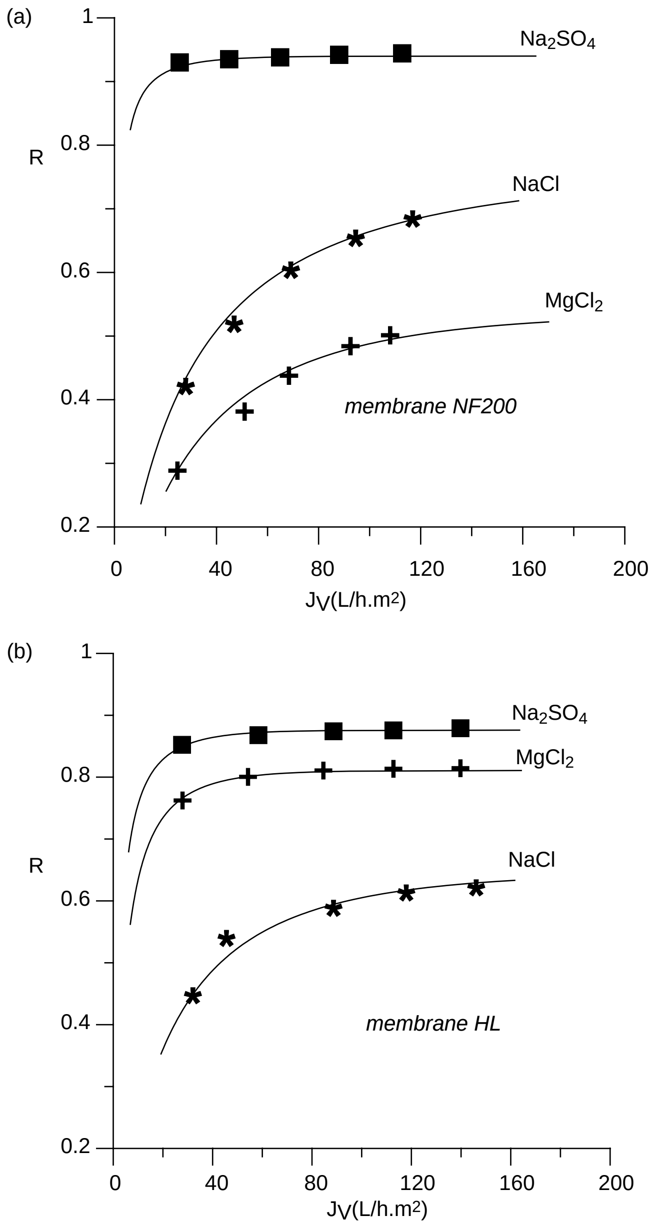


Fig. 2. Variation of salt rejection as a function of permeate flux at the feed concentration of 10^{-3} M; pH of solution 5.4. The curves were fitted by the Spiegler–Kedem model, (a) membrane NF200, (b) membrane HL.

Na_2SO_4). This study involved two sets of experiments: (1) removal of salts (NaCl, Na_2SO_4, and $MgCl_2$) as a function of permeate flux; (2) and removal of salts as a function of bulk solution concentration. From the Figs. 2 (a) and (b) we can observe two different salt retention sequence: $R(Na_2SO_4) > R(NaCl) > R(MgCl_2)$ for NF200 membrane and $R(Na_2SO_4) > R(MgCl_2) > R(NaCl)$ for HL membrane.

For NF200 membrane, a negatively charged membrane, the retention for the bivalent anion (SO_4^{2-}) is the highest, whereas that of the bivalent cation (Mg^{2+}) is the lowest and the retention of the salt with a mono-valent ion pair is in between the other two. The NF 200 membrane belongs to the category of membrane for witch Donnan exclusion seems to play an important role. Donnan effect of a membrane refers to the electrostatic interactions between ions and the membrane charge. Ions having the same sign of charge (the co-ions) as the membrane charge are excluded, whereas ions having the opposite sign of charge (counter-ions) will be attracted. a higher valence co-ion causes a higher ion retention, whereas a higher valence counter-ion leads to a lower retention of the salt [9]. For example, $R(Na_2SO_4)$ > R(NaCl), because the divalent anion, SO_4^{2-}, is strongly rejected by the negatively charged membrane compared to the mono-valent anion Cl^- (for the same counter-ion Na^+). Similarly, R(NaCl) > $R(MgCl_2)$ because Donnan exclusion results in stronger attraction of divalent counter-ions Mg^{2+} to the membrane compared to mono-valent Na^+ (for the same co-ion Cl^-).

The decrease of salts retention with increasing concentration, as can be shown in Fig. 3 (a) is in agreement with Donnan model. For HL membrane the retention is mainly caused by differences in diffusion coefficients between the different salts. As shown in Table 3, the diffusion coefficient decreases going from NaCl, $MgCl_2$ to Na_2SO_4. This order of diffusion coefficients is inversely reflected in the retention sequence. The effect of salt concentration on HL membrane rejection is shown in Fig.3 (b). In the case of single symmetric salt (NaCl), rejection decreases as the concentration increases. In the case of non-symmetric electrolytes ($MgCl_2$ and Na_2SO_4), on the contrary, rejection goes through a maximum value, as the salt concentration increases. The maximum value is located at a concentration close to 3.10^{-3} M. That quite atypical behavior in which the salt ($MgCl_2$ and Na_2SO_4) rejection increases as the salt concentration increases had been already observed by various authors for different membranes [11–14].

3.2. Nickel ions retention

In Figs. 4 (a) and (b) the retention of nickel is plotted against the permeate flux for the two membranes at different concentration. From the figures we observe that the retention of nickel is better for NF200 than for HL. Also, with increasing nickel feed concentration in the range of 10 to 100 ppm, the retention of nickel by NF200 membrane decreased from 86% to 80% while it increased from 64% to 80% in the case of HL. The decrease of nickel retention obtained by NF 200 can be related to the Donnan effect: the increase of the feed solution concentration induces the neutralization of membrane negative charges by cations. This screen formation of cations near

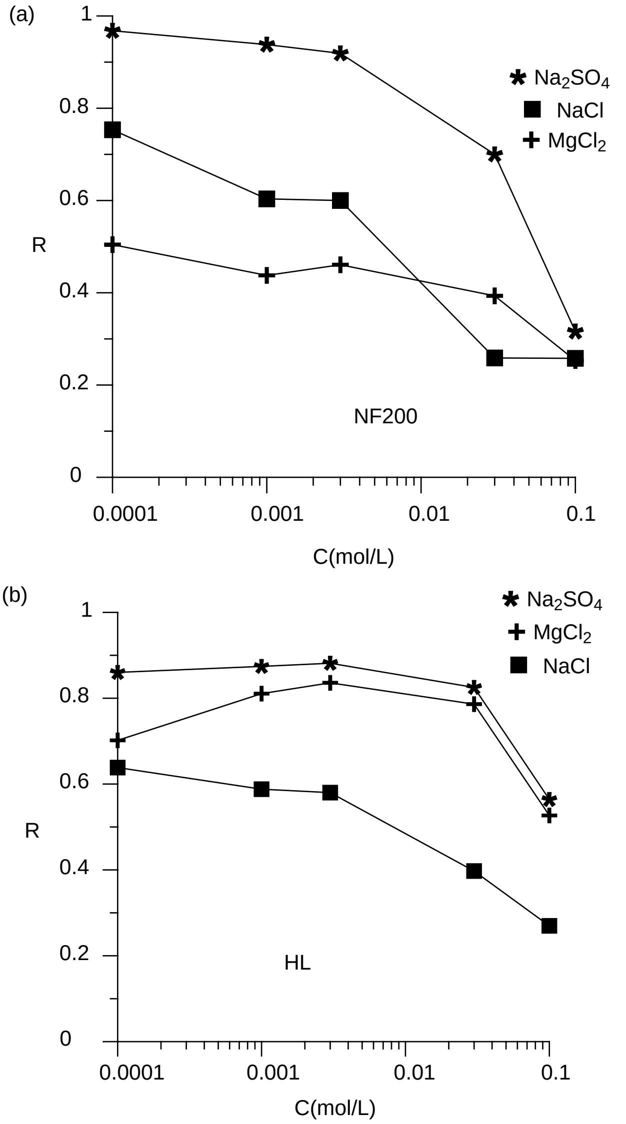


Fig. 3. Salt retention as function of concentration for different membrane at P = 7 bar; pH of solution 5.4, (a) membrane NF200, (b) membrane HL.

Table 3
Diffusion coefficients of different salts D calculated from the bulk diffusion coefficients of respective ion $D_{\text{bulk},i}$.

Salt	D (10^{-9} m^2/s)
Na_2SO_4	1.23
$MgCl_2$	1.25
NaCl	1.61

the membrane reduces the repulsion between the membrane and anions. As a result the co-ions will pass more easily through the membrane. The same results have been obtained by Murthy et al with NF-300 membrane for $NiSO_4$ retention [15] and by many NF experimental data with other solutes [16, 17].

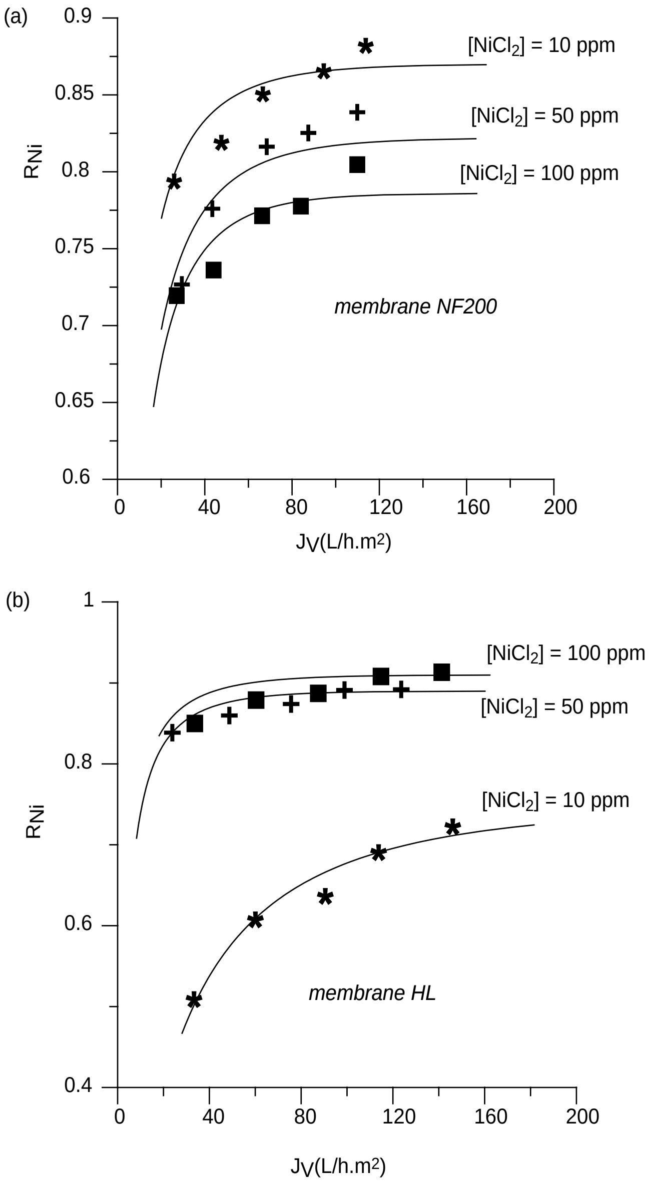
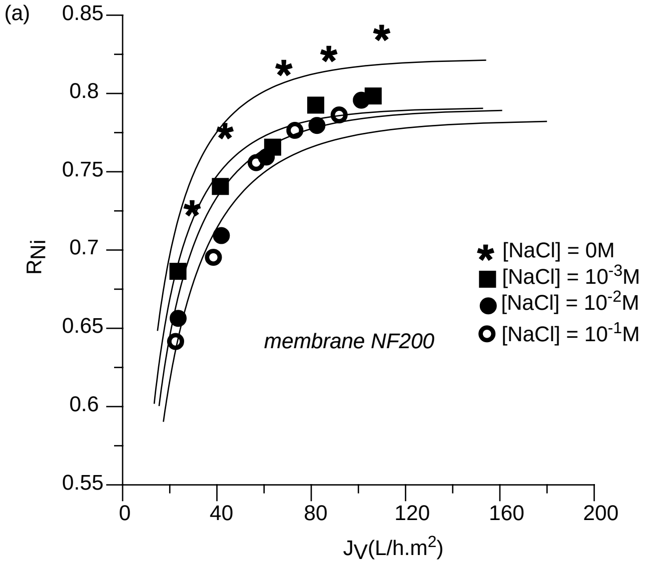


Fig. 4. Variation of Nickel rejection as a function of permeate flux at different feed concentration, pH of solution 5.4. The curves were fitted by the Spiegler–Kedem model, (a) membrane NF200, (b) membrane HL.

The increasing of retention with feed concentration obtained by HL membrane has been found by many authors [12, 18]. This result has been relating to variation of the dielectric constant, namely the dielectric exclusion, between bulk and inner membrane solutions together with its variation between solution within the pore and the membrane material. The dielectric exclusion theory recently developed by Yaroshchuk [19] is described as interaction with polarized interface, induced by the different dielectric constants, which is formally equivalent to the interaction with a fictitious image force located at the other side of the interface at the same distance from it as the real charge. It has been shown that dielectric exclusion is equivalent to a decrease in the bulk electrolyte concentration which is known to cause an increase in Donnan exclusion and that its effect is stronger in presence of multi-charge ions.

The experimental data of rejection and flux were fitted using the Spiegler–Kedem model to determine the refection (σ) and solute permeability (P_s). Solid lines in the Figs 5(a) and (b) represent Spiegler–Kedem model which confirmed that NF200 and HL membranes have a good fitting with this model. The regression parameters σ and P_s, for the two membranes under study and for different salinity levels of $NiCl_2$, are presented in Table 4. It is clear that values of σ and P_s are dependent on the salt concentration and the type of the membrane; P_s increases with salt concentration due to the high amount of salt passing through the membrane while σ slightly decreases due to the decreasing of the salt rejection.



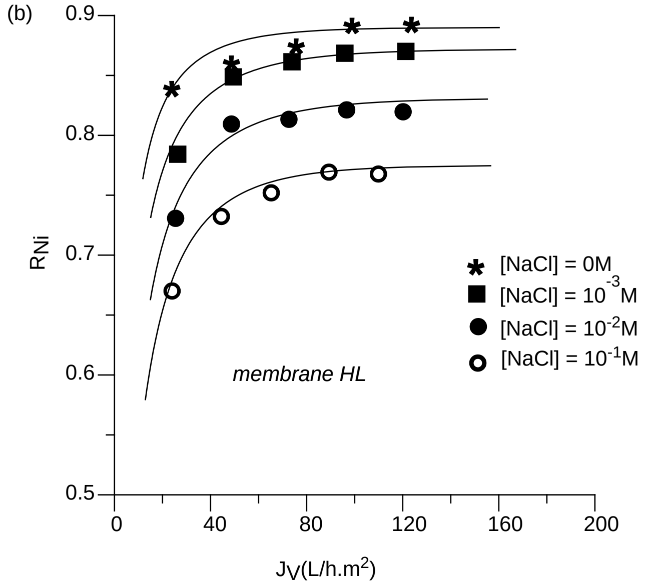


Fig. 5. Nickel rejection at different NaNO3 feed concentration as a function of permeate water flux, $[NiCl_2]$ = 50 ppm, pH of solution 5.4. The curves were fitted by the Spiegler–Kedem model, (a) membrane NF200, (b) membrane HL.

Table 4
Reflection coefficient (σ) and solute permeability (P_s) for nickel at various concentrations for two membranes.

Membrane	*NF200*		*HL*	
$[NiC1_2]$ (ppm)	σ	P_s (L/hm²)	σ	P_s (L/hm²)
10	0.864	3.78	0.745	20.1
50	0.822	5.1	0.89	2.55
100	0.786	5.17	0.91	2.35

3.2.1 Effect of ionic strength

The effect of ionic strength on nickel retention was investigated by adding different nitrate sodium salt concentrations ranging from 10^{-3} M to 10^{-1} M. The concentration of Nickel was fixed at 50 ppm. It can be seen from the Figs.5 (a) and (b) that the increase in feed salt concentration leads to a decrease of nickel retention. The decrease of nickel retention is about 5% for NF200 and 11% for HL. In fact, the increase in feed salt concentration induces a screen formation of cations (Na^+) near the membrane surface that partially neutralizes the membrane negative charges. The total charge of the membrane decrease and the co-ion (Cl^-) will easily pass through the membrane. The counter-ion will also pass freely as a result of electro-neutrality.

The solid lines in the figures are lines calculated by using the Spiegler–Kedem equation with best-fitted σ and P_s. Nickel retention have a good fitting with this model at all NaCl concentrations. The regression parameters obtained are listed in Table 5. It is clear that values of σ and P_s are dependent on the NaCl concentration; σ decreases and P_s increases with increasing NaCl concentration.

Table 5
Reflection coefficient (σ) and solute permeability (P_s) for nickel (C = 50 ppm) at different $NaNO_3$ concentrations for two membranes.

Membranes	*NF200*		*HL*	
$[NaNO_3]$ (mol/L)	σ	P_s (L/h.m²)	σ	P_s (L/h.m²)
0	0.822	5.1	0.890	2.55
10^{-3}	0.791	5.49	0.862	3.78
3.10^{-2}	0.790	7.37	0.831	4.95
10^{-1}	0.783	7.36	0.769	5.67

3.2.2 Effect of pH on nickel ions rejection

The retention of nickel ions as a function of pH values displayed in Fig.6 shows that the retention of nickel by NF200 membrane depends upon the pH value. With increasing feed pH the retention shows minima around the pH range of 4.5. This pH value is attributed to the ioselectric point (IEP). Positive charge of the membrane grows when the pH decreases and nickel ions are rejected more and more by the amide groups of the membrane. In the case of HL membrane there is no significant change in the retention of nickel ions with respect to change in feed solution pH, and this trend is observed by other researchers for the same solutes [15, 17, 19]. It can be seen from Fig. 7, the pH variation is having more effect on permeate flux with two membranes. The permeate flux reduced with increase in feed solution pH. According to Freger et al.[20] and Capelle et al.[21] the decrease of membrane permeability is due to shrinking of the skin layer due to differences of hydratation of ionised groups of the membrane.

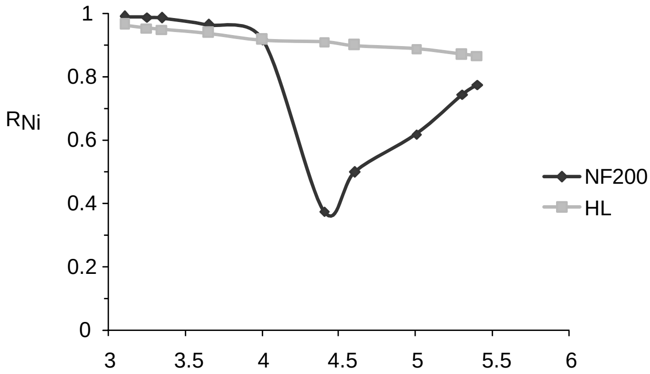


Fig. 6. Retention of Nickel salts at various pH values for different membrane, [$NiCl_2$] = 50 ppm, P = 5bar.

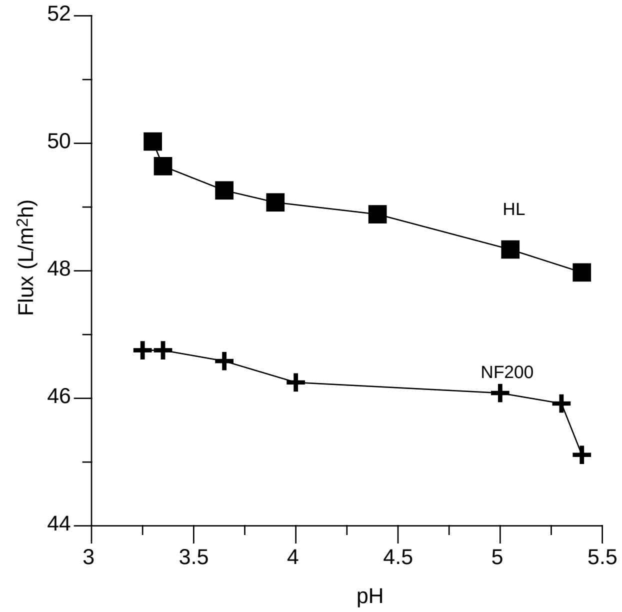


Fig. 7. Influence of pH on the permeate flux for different membrane, [$NiCl_2$] = 50 ppm, P = 5 bar.

4. Conclusion

From the results of this study, the following conclusions can be drawn:

1. The difference in salts (NaCl, Na_2SO_4, $MgCl_2$) retention sequence shows that NF200 belongs to the category of membrane for witch Donnan exclusion plays an important role while for HL the retention is mainly caused by differences in diffusion coefficients between the different salts
2. When the nickel feed concentration increased from 10 to 100 ppm, the retention of nickel by NF200 membrane decreased from 86% to 80% while it increased from 64% to 80% in the case of HL.
3. The increase in ionic strength by adding nitrate sodium salts leads to a decrease of nickel retention for the two membranes.
4. The HL membrane is less sensitive to pH in the range of pH starting than NF200
5. The Spiegler–Kedem model used to analyse the experimental data of retention versus the permeate flux showed a good fitting for all salts investigated.

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