

Comparative study of neodymium recovery from aqueous solutions by polyelectrolytes assisted-ultrafiltration

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Abstract–The Polyelectrolyte-Assisted UltraFiltration technique has demonstrated its effectiveness in the recovery of neodymium from aqueous solutions. In this study, poly(sodium 4-styrenesulfonate) and polyethylene glycol were selected as the complexing agents. The ultrafiltration experiments were operated using a laboratory scale ultrafiltration system equipped with a polyethersulfone membrane. The effects of various parameters such as polyelectrolyte concentration, applied pressure, NaCl concentration, pH and operating time on neodymium retention and permeation flux were studied. It was observed that the better result was obtained with PSS. The maximum retention was observed at 2×10^{-4} mol L⁻¹ and 3 bars for both polyelectrolytes. The results showed that the retention increased with the increase of pH. The ionic strength effect has shown a retention decrease with the increasing of salt concentration. Finally, the permeate flux declined following the increment in volume concentration factor, the retention remained constant around 98%.

Keywords: Neodymium Recovery, Polymer-assisted Ultrafiltration, Poly(sodium 4-styrenesulfonate), Polyethylene Glycol

INTRODUCTION

Rare earth elements (REEs) are used in a wide range of advanced materials. These elements are found in many interesting applications in various areas such as high-strength permanent magnets, catalysts for petroleum refining, fluorescent materials, metal and glass additives [1-3]. As a result, the widespread application of these metals results in a significant diffusion of REEs in the environment [4]. To effectively recover the REEs ions from aqueous media, various methods including chemical precipitation [5], electrochemical

treatment [6], extraction [7], and adsorption [8] have been applied.

Recently, the polyelectrolyte assisted-ultrafiltration process (PAUF) was considered as a promising alternative to conventional techniques due to its simplicity, low-energy requirement and high removal efficiency. To our best knowledge, few reports have been published so far regarding the recovery of REEs using the PAUF technique [9-14], compared to other elements such as heavy metals and dyes [15-19].

In that process, metal ions are first bound with water-soluble polymeric ligands to form macromolecular complexes, whose size

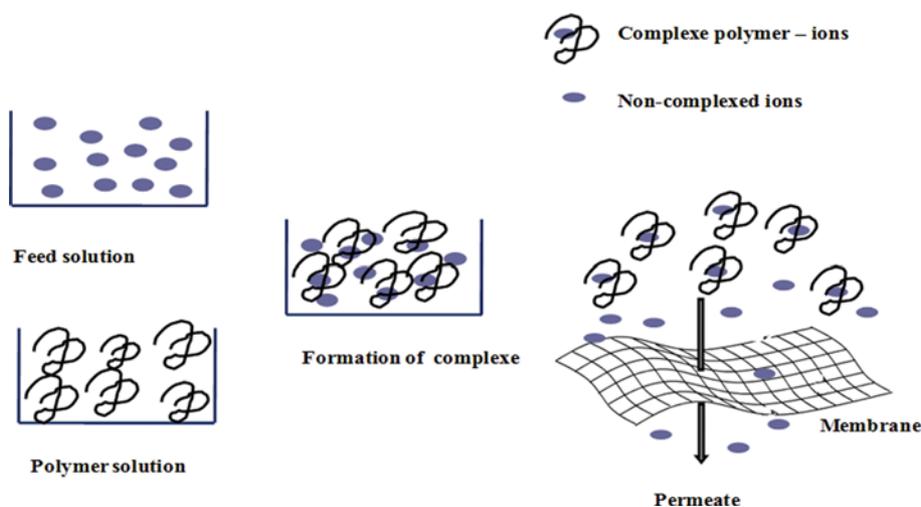


Fig. 1. Schematic of the process of metal ions recovery by PAUF technique.

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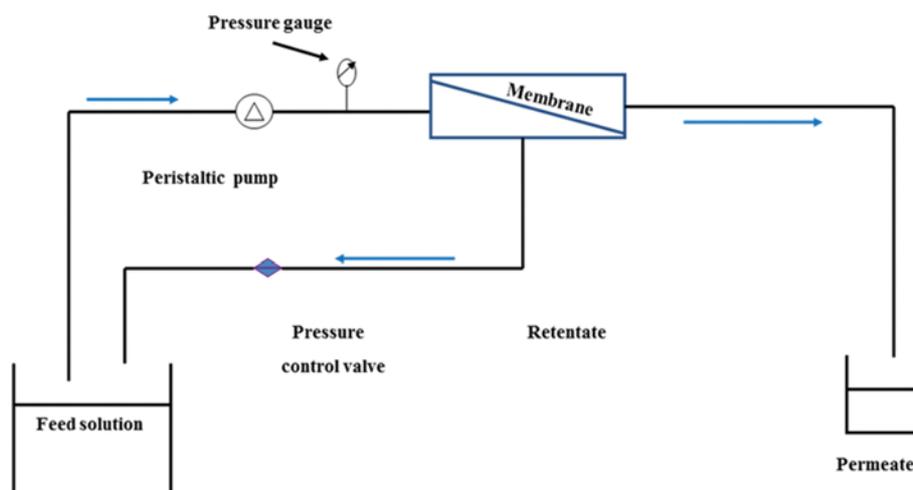


Fig. 2. Experimental ultrafiltration.

is much larger than the molecular weight cut-off (MWCO) of the UF membranes used. Then, the macromolecular complexes are retained by ultrafiltration membranes, whereas unbound metal ions pass through it, as Fig. 1 shows. As a result, a solution containing a high concentration of polymer and bound metal ions is obtained, forming the retentate or concentrate while another containing the unbound metal ions is produced, known as permeate [20]. The first experimental advances and analytical applications related to this technique were by Geckeler et al. [21,22].

The water-soluble polymer is a key component in the PAUF process. Its choice as chelating agent is an important stage. To achieve the best result, the polymer must have the following characteristics: molecular weight greater than the MWCO of the UF membranes used, sufficient solubility in aqueous solutions, high content of chelating sites or complex formation groups ("examples"; amino, imino, carboxyl and sulfonic acid groups), and high chemical and mechanical stability, low toxicity and low cost [23].

In this work, we investigated the use of the PAUF process to recover neodymium (III) from aqueous solutions. The effect of various operational parameters including transmembrane pressure, polyelectrolyte concentration, pH, operating time and salt concentration on neodymium (III) retention efficiency and permeation flux was studied. The PAUF experiments were separately conducted using two water-soluble polymers, poly(sodium 4-styrenesulfonate) (PSS) and polyethylene glycol (PEG), as the chelating agents.

MATERIALS AND METHODS

1. Materials

Commercially available poly(sodium 4-styrenesulfonate) (PSS) with molecular weight of 70 000 Da and polyethylene glycol (PEG) with molecular weight of 35 000 Da were used as the complexation agents.

The feed solutions of Nd(III) were prepared from neodymium oxide (Nd_2O_3) (Ventron 99.9%). To study the effect of pH and ionic strength on neodymium removal, sodium hydroxide, hydrochloric acid and chloride sodium were respectively used. All reagents were of analytical grade and supplied by Sigma Aldrich.

Dilutions and preparation of feed solutions involved using ultra-pure water produced by Milli-Q gradient unit (Millipore).

2. Ultrafiltration Process

Filtration experiments were carried out with a tangential cell system (Millipore Labscale TFF), using a 10 000 Da molecular weight cut-off polyethersulfone (PES) membrane from Millipore (Germany). The membrane was 0.188 cm length, with a 0.005 m² effective filtration area. At the beginning of each experiment, the inlet flux was kept constant (up to 0.5 m s⁻¹) and a transmembrane pressure was varied from 1 to 3 bars. All ultrafiltration experiments were at room temperature (25 °C). Fig. 2 represents the experimental ultrafiltration system, which was employed during the present study.

The permeation flux (J_v) was measured by determining the permeate volume produced in a period of time and calculated using the following equation:

$$J_v = \frac{V_p}{S \times t} \quad (1)$$

where J_v refers to the permeation flux (L h⁻¹m⁻²), V_p (L) represents the volume of the permeate sample collected over a period of time t (h) through an effective membrane surface area S (m²). The volume concentration factor (VCF) was evaluated using the following equation:

$$\text{VCF} = \frac{V_{ini}}{V_{ret}} \quad (2)$$

where V_{ini} and V_{ret} are the volume of the feed and the retentate solution, respectively.

The efficiency of the membrane filtration process was determined by the evaluation of the retention coefficients R (%) by means of the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p refers to the neodymium concentration (mol L⁻¹) in the permeate sample and the concentration of the neodymium in the feed solution (mol L⁻¹) is defined by C_f .

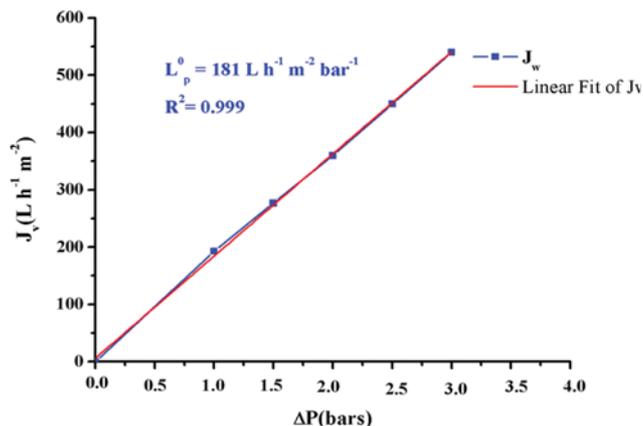


Fig. 3. Permeate flux of water as a function of transmembrane pressure.

3. Chemical Analysis

The neodymium concentration, especially for the determination of retention values, was analyzed using the inductivity coupled plasma optical emission spectrometer (ICP-OES) (optima 7300 V). Each sample was analyzed three times to get an average concentration value. A pH meter (Metrohm 654) was used for measuring the pH of feed and permeate solutions throughout the study.

4. Membrane Characterization

The performance of a membrane is strongly related to its pure water permeability (L_p^0). Before each experiment, the (L_p^0) of the membrane (defined as pure water flux (J_w)/applied pressure difference (ΔP)) was evaluated to characterize the membrane. By plotting membrane flux (J_w) for a variation of applied pressure (ΔP), the pure water permeability (L_p^0) can be obtained from the slope of the straight line, as shown in Fig. 3. In the present case, for PES-10 membrane, the pure water permeability (L_p^0) was found to be 181 ($L h^{-1} m^{-2} bar^{-1}$), which was in the range of ultrafiltration membranes. This value was considered as a reference to evaluate cleaning procedure, concentration polarization and fouling phenomenon.

After each experiment, the membrane was rinsed with ultra-pure water for 30 min at 3 bars to prevent concentration polarization and retain its performance. The membrane was used for a new filtration only when the deviation of pure water flux was low.

Using the permeability value obtained, the hydraulic resistance R_m (m^{-1}) of the membrane was calculated via the following equation:

$$J_w = L_p^0 \Delta P = \frac{\Delta P}{\eta^0 \times R_m} \quad (4)$$

where J_w represents the pure water flux, L_p^0 refers to the permeability of solvent. It depends on the solvent viscosity (η^0), and morphologic characteristics of membrane (porosity, specific surface, etc). ΔP denotes the transmembrane pressure and R_m refers to the hydraulic membrane resistance (m^{-1}). The resulting membrane resistance has a value of $2.5 \times 10^{12} m^{-1}$.

RESULTS AND DISCUSSION

1. Ultrafiltration of Aqueous Solutions of Nd(III)

Fig. 4 depicts the permeate flux and neodymium retention as a

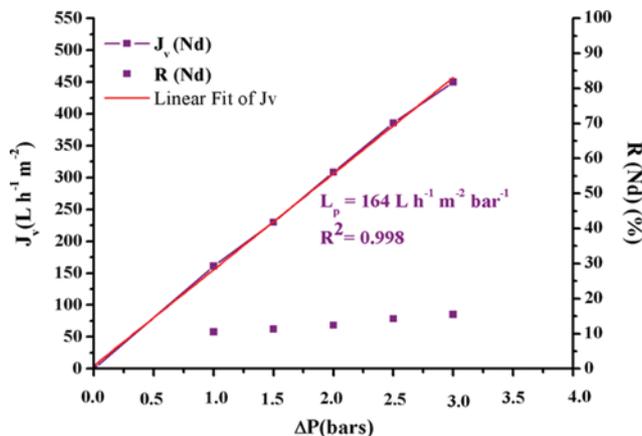


Fig. 4. Neodymium retention and permeate flux as a function of transmembrane pressure, $[Nd^{3+}] = 10^{-4} mol L^{-1}$.

function of the transmembrane pressure for a feed neodymium concentration equal to $10^{-4} mol L^{-1}$. As can be seen from this figure, the retention remained nearly constant at the value of 15%. Neodymium ions retention was low. To improve this retention, there is a growing interest in developing and optimizing an alternative and promising method for the recovery of rare earth from aqueous solutions. In this regard, the ultrafiltration assisted by polyelectrolyte (PAUF) has received considerable attention. Two different water-soluble polymers (PSS and PEG) were used as a complexing agent to study the PAUF in the removal of neodymium (III). The PSS was selected because its average acidity constant, pKa, is as low as 1. Therefore, this polyelectrolyte remains predominantly anionic over a wide pH range, which thereby facilitates the interaction of the polymeric chains with the positively charged ions Nd (III) [24-26]. PEG is a non-ionic polymer whose interaction with metals ions can occur by physical adsorption [27,28]. The purpose of using PEG is to compare its recovery performance to that obtained with PSS.

As it can be observed in Fig. 4, there is a linear dependence of neodymium solution permeate flux (J_v) with transmembrane pressure ΔP . The slope of the straight line is the aqueous neodymium permeability ($L_p = 164 L h^{-1} m^{-2} bar^{-1}$). Note that the difference in pure water membrane permeability ($L_p^0 = 181 L h^{-1} m^{-2} bar^{-1}$) and neodymium ions permeability is not important.

Hydraulic total resistance has a value of $3.13 \times 10^{12} m^{-1}$. From this value, the presence of neodymium ions does not generate some significant additive resistance, generally manifested when solutes are filtered through the membrane.

2. Effect of the Polyelectrolyte Concentration on Neodymium Retention and Permeate Flux in PAUF Process

The effect of polyelectrolyte concentration on neodymium retention and permeate flux is illustrated in Fig. 5(a) and Fig. 5(b), respectively. This operating parameter was studied at a fixed neodymium concentration of $10^{-4} mol L^{-1}$ and with polyelectrolyte concentration ranging from 0 to $10^{-3} mol L^{-1}$. In the absence of polyelectrolyte, the neodymium retention was low and did not exceed 15%, but it exhibited a reasonable enhancement, following the increase in polyelectrolyte concentration, as shown in Fig. 5(a).

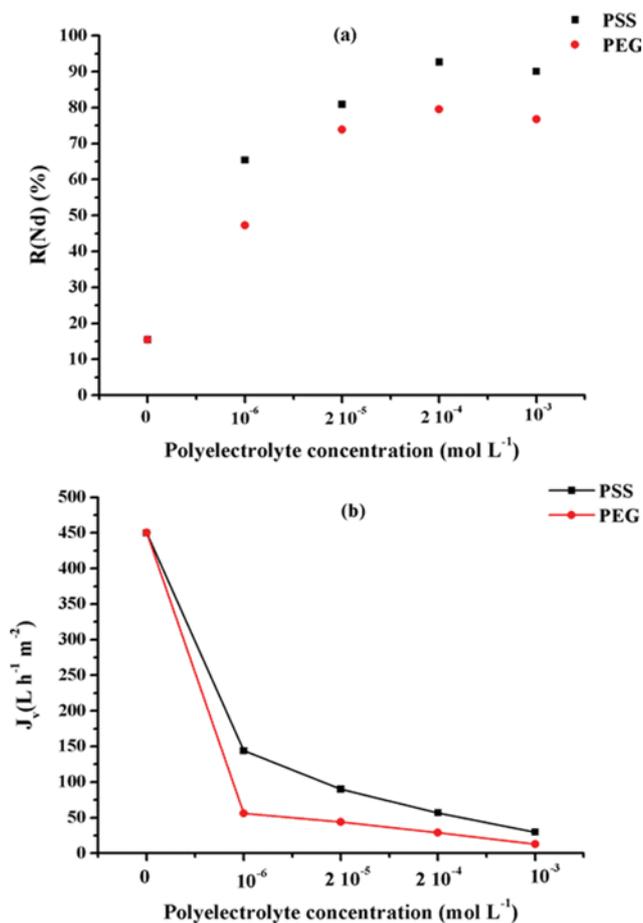


Fig. 5. Effect of polyelectrolyte concentration on (a) neodymium retention and (b) permeation flux ($[\text{Nd}^{3+}] = 10^{-4} \text{ mol L}^{-1}$, $\Delta P = 3 \text{ bars}$).

The increasing neodymium retention can be explained by the fact that an increment in polyelectrolyte concentration usually leads to an increase in the number of available binding sites; this, in turn, favors the interaction between the neodymium ions and the binding sites on the polyelectrolyte chain. The neodymium retention attained a maximum value of 93% in the case of PSS and 75% in the case of PEG, at polyelectrolyte concentration of $2 \times 10^{-4} \text{ mol L}^{-1}$, and after that it decreased with the further increase of polyelectrolyte concentration, which indicated that the complexation phenomenon had reached a dynamic equilibrium at this concentration. In the rest of study, we chose $2 \times 10^{-4} \text{ mol L}^{-1}$ of polyelectrolyte as optimum concentration. Note that when PSS was used as the chelating agent, the neodymium retention was higher than that obtained using PEG.

The rejection of neodymium ions using a commercial nanofiltration (NF) membrane was also investigated by Murthy et al. [29]. In this work, an anionic surfactant sodium dodecyl sulphate (SDS) and a chelating agent ethylenediaminetetraacetic acid (EDTA) were used to increase the neodymium ions rejection. They reported that the addition of (SDS) and (EDTA) would enhance the rejection efficiency of Nd (III) ions from 86.74% to 99.45% and 99.36%, respectively. Some researchers recovered neodymium ions by other methods, such as adsorption. Gasser et al. [30] used the Mg-Fe-

LDH-Cyanex-272 as an adsorbent for the recovery of neodymium ions. They concluded that the recovery percent of Nd (III) ions from the spent battery was found to be about 98%. The separation of rare earth elements from aqueous solution using graphene oxide GO has also been reported. The obtained results exhibited an excellent adsorption performance for La (III), Nd (III), G (III) and Y (III). A high adsorption capacity of REEs in the following order $\text{G (III)} > \text{Nd (III)} > \text{Y (III)} > \text{La (III)}$ (255.5, 188.6, 135.7 and 85.7 mg/g) was achieved [31].

Fig. 5(b) similarly illustrates the variations in permeation flux, as a function of polyelectrolyte concentration. As shown in Fig. 5(b), permeation flux demonstrated a downward trend for both the polyelectrolytes. The flux decreases from 450 to $29.75 \text{ L h}^{-1} \text{ m}^{-2}$ in the case of PSS and from 450 to $12.85 \text{ L h}^{-1} \text{ m}^{-2}$ in the case of PEG. That may be attributed to the effect of the concentration polarization phenomenon at the membrane surface, which imposes a hydrodynamic resistance to mass transport through the membrane, thereby lowering the permeation flux. A similar result was also observed in our previous study [32]. Another explanation of the reduction observed in permeation flux is the increase in the limit viscosity of the polymer solution, following the augmentation in polymer concentration. This leads inadvertently to a reduction of the critical concentration of entanglement, as a result of the fact that the limit viscosity is inversely proportional to the concentration of entanglement. An increase in the polymer concentration reduces this concentration of entanglement; therefore, the interaction between the uncharged polymer chains increases, resulting in the formation of a gel layer at the surface of the membrane, which subsequently decreases the permeation flux [33,34].

3. Effect of Transmembrane Pressure on Neodymium Retention and Permeation Flux

The evolution of neodymium and permeate flux with transmembrane pressure was investigated in the pressure range from 0 to 3 bars. The Nd(III) and polyelectrolyte concentration were taken as 10^{-4} and $2 \times 10^{-4} \text{ mol L}^{-1}$, respectively. The results obtained are shown in Fig. 6(a) and Fig. 6(b), respectively. From Fig. 6(a) one can note that there is an increase of neodymium retention with the increase of transmembrane pressure. A maximum retention was observed at 3 bars transmembrane pressure for both polyelectrolytes.

As regards the permeation flux response, it was shown that an enhancement of transmembrane pressure, which was the primary driving force for mass transfer in the present case has a favorable effect on the permeate flux for both polyelectrolytes. Thus, an increase in the transmembrane pressure resulted in a dramatic enhancement in the effective driving force for mass transfer, thereby augmenting the convective transport of the solvent water to the membrane, accompanied by the solute molecules, to the membrane, leading to a dramatic improvement in permeate flux [35].

Besides, by comparing the permeate flux observed during ultrafiltration of neodymium in the presence of the polyelectrolyte with that of pure water (Fig. 3), we note that the neodymium fluxes show a decrease. This observation can be attributed to the concentration polarization and the gel layer formation that results in the decrease of permeate flux. This trend is well known for the driven pressure process.

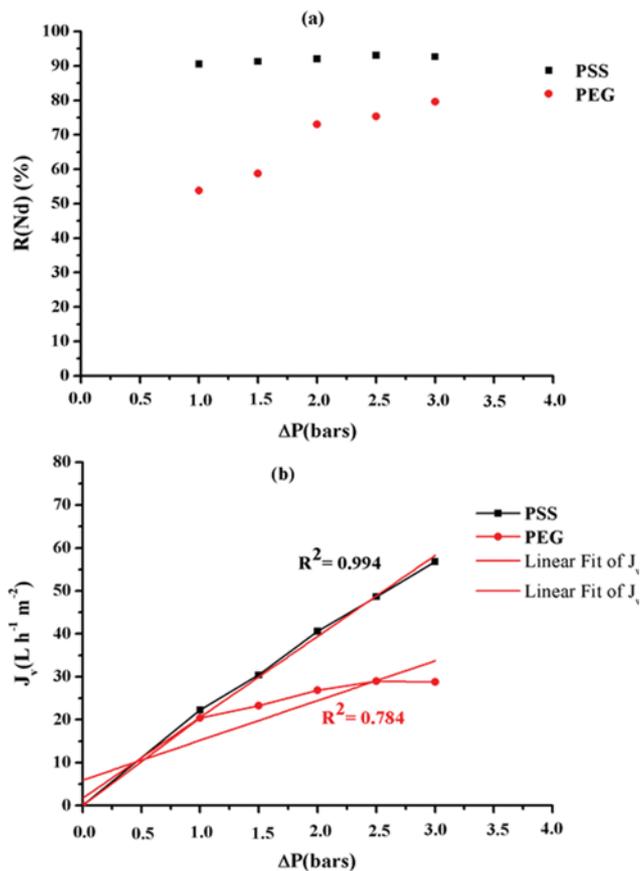


Fig. 6. Effect of transmembrane pressure on (a) neodymium retention and (b) permeation flux ($[\text{Nd}^{3+}] = 10^{-4} \text{ mol L}^{-1}$, polyelectrolyte concentration = $2 \times 10^{-4} \text{ mol L}^{-1}$).

4. Effect of the pH Solution

One of the most important factors involved in the interaction of metal ions with polymers is the pH of the solution [36]. This parameter affects the effectiveness of the retention of metal ions by PAUF process [37]. Fig. 7(a) and Fig. 7(b) show the variation of neodymium retention and permeate flux as a function of pH ranging from 1 to 9. In this study, the concentrations of neodymium and polyelectrolyte were fixed at 10^{-4} and $2 \times 10^{-4} \text{ mol L}^{-1}$, respectively. The transmembrane pressure was kept constant at 3 bars.

As Fig. 7(a) demonstrates, the neodymium retention increases with the increment in pH for both the polyelectrolytes. In the case of PSS, the highest percentage retention of neodymium (99%) occurred at pH 6, while in the case of PEG, the best retention (86%) was achieved at pH 8.

At lower pH values, the concentration of hydrogen ions was found to be higher, thereby leading to the competition of those ions with neodymium. So the interaction between metal ions and polymer decreased, which makes neodymium retention reduced significantly. Following the increase in pH values, the concentration of hydrogen ions decreases. As a result, the binding sites of polymer towards the neodymium ions increase and, consequently, the formation of the complex Nd-polyelectrolyte is improved, which leads to the increase of $R(\text{Nd})$ [10].

By comparing the profile of neodymium retention for both poly-

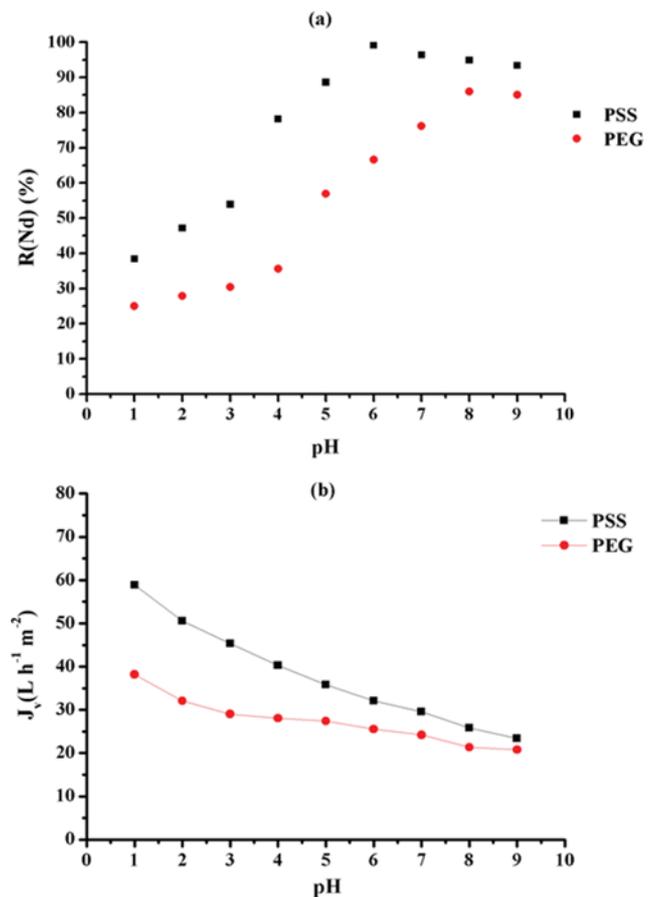


Fig. 7. Effect of pH on (a) neodymium retention and (b) permeation flux ($[\text{Nd}^{3+}] = 10^{-4} \text{ mol L}^{-1}$, polyelectrolyte concentration = $2 \times 10^{-4} \text{ mol L}^{-1}$, $\Delta P = 3 \text{ bars}$).

electrolytes PSS and PEG, we note that the retention of neodymium with PSS is more sensitive with changing pH. Also, the obtained retention values in the presence of PSS seem to be greater than those obtained in the presence of PEG. This phenomenon is explained probably as follows: the interaction between neodymium ions and the negatively charged sulfonate groups on the PSS chain could be considered as predominantly electrostatic [38]. This electrostatic interaction and the subsequent complexation of the cationic ions to the anionic sites on the polyelectrolyte backbone are, moreover, increased progressively, following the increase pH values. However, in the case of PEG, neodymium ions are bound to the surface of the non-ionic PEG by physical adsorption [28]. Then, we can conclude that the difference in the profile of retention for both polyelectrolytes may be due to the difference in the type of interaction involved between Nd (III) ions and polyelectrolytes used in this study.

From Fig. 7(b), it is seen that there is a reduction of permeate flux with pH. This result is presumably due to the changes in structural conformation of polymer molecules with pH as a result of neutralization of polymer charge by means of their interaction with the cationic neodymium ions. These changes in polymer configuration can produce a fouling phenomenon by pore blocking, which results in the observed decrease in permeate flux [39].

5. Effect of the Added Salt

The effectiveness of polymer-assisted ultrafiltration process can be strongly influenced by the ionic strength of the aqueous solutions [40]. Increasing the salt concentration leads to the compression of the electrical double layer and thus to a reduction in the electrostatic attraction between ions and charged polymers. Thereby, resulting in lower metals' retention efficiency owing to the unhindered passage of the unbound metals through the membrane [41].

The effect of ionic strength of the solution on the retention of Nd(III) and permeate flux in the presence of PSS and PEG is shown in Fig. 8(a) and Fig. 8(b), respectively. Ultrafiltration experiments were conducted with an applied pressure of 3 bars, neodymium concentration and polyelectrolyte concentration of 10^{-4} and 2×10^{-4} mol L $^{-1}$, respectively, and pH value of 6 for PSS and 8 for PEG. The concentration of NaCl in these experiments varied from 10^{-5} to 10^{-1} mol L $^{-1}$. As can be observed in Fig. 8(a), the increase in salt concentration is followed by a reduction in the Nd (III) retention. In the case of PSS, the retention values change from 99% to 65% upon increasing the sodium chloride concentration from 10^{-5} to 10^{-1} mol L $^{-1}$. The phenomenon can be attributed mainly to the competition of Na $^{+}$ with positively charged neodymium ion for the same binding sites on the polyelectrolyte surface, and as a consequence, reducing the electrostatic attraction between the

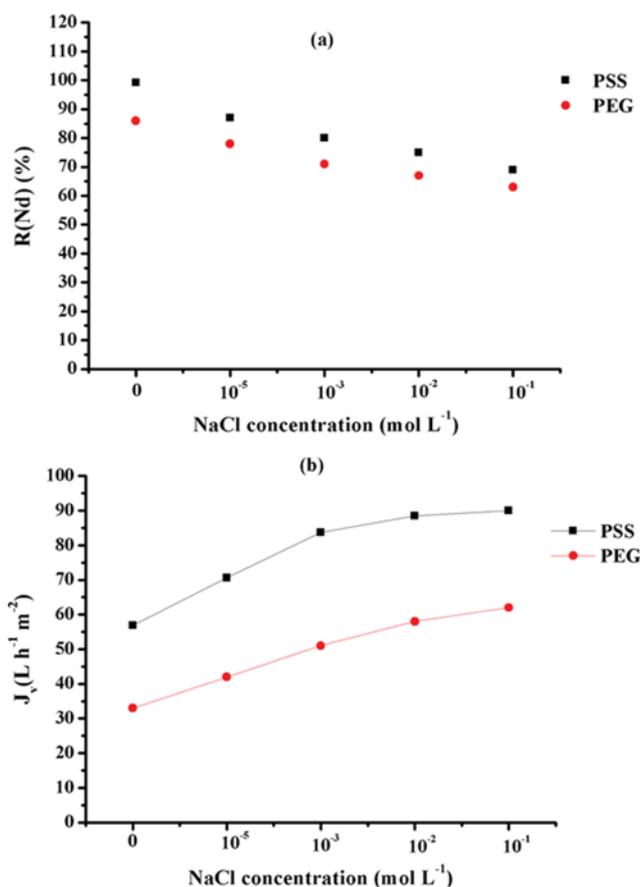


Fig. 8. Effect of salt concentration on (a) neodymium retention and (b) permeation flux ($[\text{Nd}^{3+}] = 10^{-4}$ mol L $^{-1}$, polyelectrolyte concentration = 2×10^{-4} mol L $^{-1}$, pH = 6 and 8 for Nd-PSS and Nd-PEG, respectively, $\Delta P = 3$ bars).

polyelectrolyte and the Nd(III). This should reduce the probability of the formation of some complexes between the PSS and the neodymium ions.

In the case of PEG, neodymium retention decreased slightly upon increasing the NaCl concentrations. This low decrease of retention can support the hypothesis that the complex formed in this case is not electrostatic.

The influence of ionic strength on the permeate flux is presented in Fig. 8(b). From this figure, we note that permeate flux tends to increase with the increment of salt concentration from 10^{-5} to 10^{-1} mol L $^{-1}$. It increases from 70.58 to 90 L h $^{-1}$ m $^{-2}$ for the PSS and from 42 to 62 L h $^{-1}$ m $^{-2}$ in the presence of PEG. In fact, this enhancement in permeate values could be attributed to the change in polyelectrolyte conformation as a result of neutralization of anionic sites of polymer, which would weaken the interaction between neodymium ions and the polyelectrolyte. This is in good agreement with what Ennigrou et al. [42] observed for the Cd(II) retention assisted by poly(ammonium acrylate) (PANH $_4$) as a complexing agent. They noted that following the increase in NaNO $_3$ concentration, the permeate flux decreased.

6. Concentration Experiments

As the PSS gives better results than the PEG, it was selected for the concentration experiments. The experiment was tested at the constant operating conditions determined in previous sections (a fixed Nd $^{3+}$ concentration of 10^{-4} mol L $^{-1}$, [PSS] of 2×10^{-4} mol L $^{-1}$, pH of 6 and transmembrane pressure of 3 bars). The effect of volume concentration factors (VCF) on R (Nd) and J_v is presented in Fig. 9. One can note that there is a decrease of permeate flux with the enhancement of VCF. During the concentration process, J_v values are significantly reduced from 27.19 to 14.28 L h $^{-1}$ m $^{-2}$. In fact, this decrease in permeation flux values could be attributed to the insignificant concentration polarization, which is in agreement with the results obtained by Zeng et al. [43]. In contrast to permeate flux, the retention remains independent of VCF. It always reaches a limiting value of 98%, whatever is the value of the VCF as shown in Fig. 9.

When the volume concentration factor reaches the value of 6.25, the concentration of neodymium in the retentate achieved its maxi-

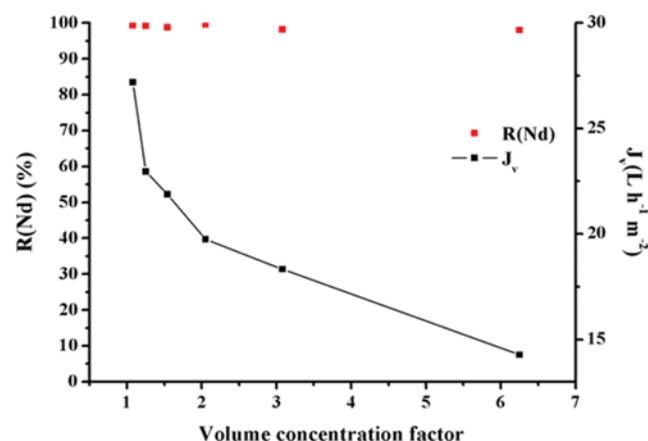


Fig. 9. Effect of volume concentration factor (VCF) on neodymium retention and permeation flux ($[\text{Nd}^{3+}] = 10^{-4}$ mol L $^{-1}$, [PSS] = 2×10^{-4} mol L $^{-1}$, pH = 6, $\Delta P = 3$ bars, feed volume = 0.5 L).

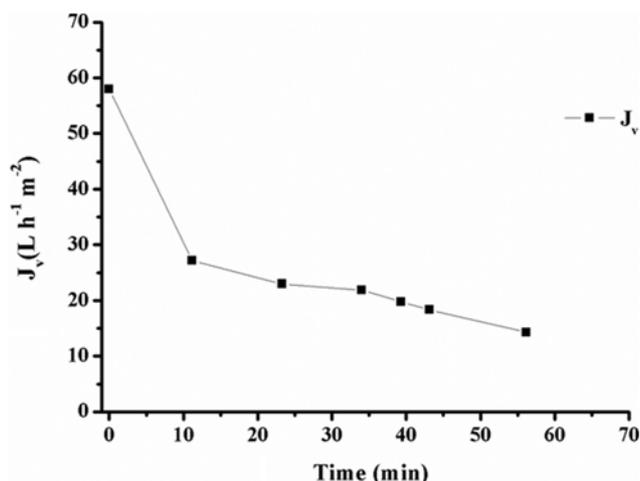


Fig. 10. Effect of time on permeation flux ($[Nd^{3+}] = 10^{-4} \text{ mol L}^{-1}$, $[PSS] = 2 \times 10^{-4} \text{ mol L}^{-1}$, $pH = 6$, $\Delta P = 3 \text{ bars}$).

mum which was 699.8 mg L^{-1} . However, it was 4.14 mg L^{-1} in the permeate.

On the other hand, the effect of operating time on permeation flux is shown in Fig. 10. By analyzing this figure, we note that the permeation flux depended strongly on the operating time. It demonstrates a downward trend. The permeate flux drops from 58 to $27.19 \text{ L h}^{-1} \text{ m}^{-2}$ when the operating time varies from 0 to 11.2 min, then declines until reaching $14.28 \text{ L h}^{-1} \text{ m}^{-2}$ after an operating time of 56.17 min. This could account for the phenomenon of the accumulation of retained solute and polymer aggregates in the immediate vicinity of the membrane surface. As a result, the concentration polarization effect can be dominant and membrane selectivity decreases [44–46].

CONCLUSIONS

Poly(sodium 4-styrenesulfonate) (PSS) and polyethylene glycol (PEG) were suitably selected as the accompanying complexing polymers. PSS showed the best performance in neodymium recovery from aqueous solutions (99%).

The transmembrane pressure and concentration of polyelectrolyte have an effect on the retention and permeate flux. It was found that the retention increases with increasing pressure and concentration of the polyelectrolyte. The optimum polyelectrolyte concentration and transmembrane pressure were determined as $2 \times 10^{-4} \text{ mol L}^{-1}$ and 3 bars, respectively. While, permeation flux increases linearly with transmembrane pressure and decreases with the increment of polyelectrolyte concentrations.

Results indicate that the recovery of neodymium ions using PAUF process was highly dependent on the pH values. It was also observed that an increment in pH would increase the neodymium retention to a great extent, but it would drop the permeate flux. In the case of PSS, the highest percentage retention of neodymium (99%) occurred at pH 6, while in the case of PEG, the best retention (86%) was achieved at pH 8.

The study of the concentration process revealed that the permeation flux was significantly influenced by the variation of the vol-

ume concentration factor (VCF), but any change on the neodymium retention was observed. It was shown that the Nd-PSS complex can be effectively concentrated and future work will be focused on the regeneration of the polymer for reuse in the PAUF process.

NOMENCLATURE

REEs : rare earth elements

PAUF : polyelectrolyte-assisted ultrafiltration

MWCO : molecular weight cut-off

UF : ultrafiltration

PSS : poly(sodium 4-styrenesulfonate)

PEG : polyethylene glycol

Da : dalton

Nd(III) : neodymium(III)

PES : polyethersulfone membrane

J_v : permeate flux [$L h^{-1} m^{-2}$]

V_p : volume of permeate [mL]

t : time [h]

S : effective membrane area [m^2]

VCF : volume concentration factor

V_{ini} : volume of the feed solution

V_{ret} : volume of the retentate solution

R(%) : neodymium retention

C_p : neodymium concentration in permeate sample [$mol L^{-1}$]

C_f : neodymium concentration in feed solution [$mol L^{-1}$]

ICP-OES : inductivity couple plasma optical emission spectrometer

L_p^0 : pure water permeability [$L h^{-1} m^{-2} bar^{-1}$]

J_w : pure water flux [$L h^{-1} m^{-2}$]

ΔP : transmembrane pressure [bar]

R_m : hydraulic membrane resistance [m^{-1}]

η^0 : solvent viscosity

L_p : permeability of aqueous neodymium solutions [$L h^{-1} m^{-2} bar^{-1}$]

$[Nd^{3+}]$: concentration of neodymium [$mol L^{-1}$]

Cd(II) : cadmium(II)

PANH₄ : poly(ammonium acrylate)

[PSS] : concentration of poly(sodium 4-styrenesulfonate)

REFERENCES

1. A. R. Chakmouradian and F. Wall, *Elements*, **8**, 333 (2012).
2. M. A. Alam, L. Zuga and M. G. Pecht, *Ceram. Int.*, **38**, 6091 (2012).
3. B. L. Rivas, J. Sánchez and B. F. Urbano, *Polym. Int.*, **65**, 255 (2016).
4. R. Chi and J. Tian, *Weathered crust elution-deposited rare earth ores*, Nova Science Publishers, New York (2008).
5. R. D. Abreu and C. A. Morais, *Miner. Eng.*, **23**, 536 (2010).
6. S. Vasudevan, G. Sozhan, S. Mohan and S. Pushpavanam, *Hydrometallurgy*, **76**, 115 (2005).
7. R. Banda, H. Jeon and M. Lee, *Sep. Purif. Technol.*, **98**, 481 (2012).
8. L. Hadjittofi, S. Charalambous and I. Pashalidis, *J. Rare Earths*, **34**, 99 (2016).
9. G. E. Chen, D. Sun and Z. L. Xu, *Adv. Mater. Res.*, **233**, 959 (2011).
10. J. Zeng, Q. He, H. Zhou, X. Sun and J. Zhang, *Asia-Pacific J. Chem. Eng.*, **7**, 940 (2012).
11. M. V. Norton, F. A. DiGiano and R. T. Hallen, *Water Environ. Res.*,

- 69, 244 (1997).
12. M. Hammami, D. J. Ennigrou, K. H. Naifer and M. Ferid, *Desalin. Water Treat.*, **56**, 2715 (2015).
 13. M. Hammami, D. J. Ennigrou, K. H. Naifer and M. Ferid, *Environ. Prog. Sustain. Energy*, **35**, 1091 (2016).
 14. V. Ramachandhran, S. K. Samanta and B. M. Misra, *J. Radioanal. Nucl. Chem.*, **237**, 121 (1998).
 15. Y. H. Chou, K. H. Choo, S. S. Chen, J. H. Yu, C. Y. Peng and C. W. Li, *Sep. Purif. Technol.*, (2017). (in press).
 16. C. Haktanir, H. Ö. Özbelge, N. Bıçak and L. Yılmaz, *Sep. Sci. Technol.*, 1520, Posted Online 22 June (2017).
 17. Y. Huang, J. Du, Y. Zhang, D. Lawless and X. Feng, *J. Membr. Sci.*, **514**, 229 (2016).
 18. M. Palencia, J. M. Martínez and Á. Arrieta, *J. Sci. Technol. Appl.*, **2**, 65 (2017).
 19. J. H. Yu, Y. H. Chou, Y. M. Liang and C. W. Li, *Water Sci. Technol.*, **72**, 1096 (2015).
 20. R. Molinari, P. Argurio, T. Poerio and G. Gullone, *Desalination*, **200**, 728 (2006).
 21. K. E. Geckeler, E. Bayer, B. Y. Spivakov, V. M. Shkinev and G. A. Vorobëva, *Anal. Chim. Acta*, **189**, 285 (1986).
 22. E. Geckeler, *Pure Appl. Chem.*, **73**, 129 (2001).
 23. K. E. G. L. Geckeler, G. Lange, H. Eberhardt and E. Bayer, *Pure Appl. Chem.*, **52** 1883 (1980).
 24. B. L. Rivas, E. D. Pereira, M. Palencia and J. Sánchez, *Prog. Polym. Sci.*, **36**, 294 (2011).
 25. B. L. Rivas and I. Moreno-Villoslada, *J. Appl. Polym. Sci.*, **70**, 219 (1998).
 26. I. Korus, *Polimery*, **55**, 135 (2010).
 27. M. Al-Hwaiti, K. A. Ibrahim and M. Harrara, *Arabian J. Chem.*, (2015), Available Online 11 August (2015).
 28. N. H. Baharuddin, N. M. N. Sulaiman and M. K. Aroua, *J. Environ. Health Sci. Eng.*, **12**, 61 (2014).
 29. Z. V. P. Murthy and A. Choudhary, *J. Rare Earths*, **29**, 974 (2011).
 30. M. S. Gasser and M. I. Aly, *Int. J. Miner. Process.*, **121**, 31 (2013).
 31. R. M. Ashour, H. N. Abdelhamid, A. F. Abdel-Magied, A. A. Abdel-Khalek, M. M. Ali, A. Uheida, M. Muhammed, X. Zou and J. Dutta, *Solvent Extr. Ion Exch.*, **35**, 91 (2017).
 32. X. Zhu and K. H. Choo, *Colloids Surf., A: Physicochem. Eng. Asp.*, **312**, 231 (2008).
 33. S. Chakraborty, J. Dasgupta, U. Farooq, J. Sikder, E. Drioli and S. Curcio, *J. Membr. Sci.*, **456**, 139 (2014).
 34. E. P. Kuncoro, J. Roussy and E. Guibal, *Sep. Sci. Technol.*, **40**, 659 (2005).
 35. J. Dasgupta, M. Singh, J. Sikder, V. Padarthy, S. Chakraborty and S. Curcio, *Ecotoxicol. Environ. Saf.*, **121**, 271 (2015).
 36. P. Cañizares, A. Pérez, R. Camarillo and R. Mazarro, *J. Membr. Sci.*, **320**, 520 (2008).
 37. S. İslamoğlu and L. Yılmaz, *Desalination*, **200**, 288 (2006).
 38. B. L. Rivas, E. D. Pereira, M. Palencia and J. Sánchez, *Prog. Polym. Sci.*, **36**, 294 (2011).
 39. H. Hoffmann, K. Kamburova, H. Maeda and T. Radeva, *Colloids Surf., A: Physicochem. Eng. Asp.*, **354**, 61 (2010).
 40. A. Tabatabai, J. F. Scamehorn and S. D. Christian, *Sep. Sci. Technol.*, **30**, 211 (1995).
 41. R. S. Juang and R. C. Shiau, *J. Membr. Sci.*, **165**, 159 (2000).
 42. D. J. Ennigrou, L. Gzara, M. R. B. Romdhane and M. Dhahbi, *Chem. Eng. J.*, **155**, 138 (2009).
 43. J. Zeng, S. Li, X. Sun and X. Chen, *Chem. Eng. Technol.*, **35**, 387 (2012).
 44. B. K. Dutta, Principles of Mass Transfer and Separation Processes, PHI Learning Pvt., Ltd., New Delhi (2007).
 45. P. Cañizares, A. de Lucas, Á. Pérez and R. Camarillo, *J. Membr. Sci.*, **253**, 149 (2005).
 46. D. Zamariotto, B. Lakard, P. Fievet and N. Fatin-Rouge, *Desalination*, **258**, 87 (2010).