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Retention of samarium ions from aqueous solutions by poly(acrylic acid)-enhanced ultrafiltration

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ABSTRACT

Rare earth elements (REE) are widely used in variety of commercial applications, which results in public exposure to them, and it is a matter of concern. Recent studies have demonstrated that the toxicity of (REE) as a group is similar to the toxicity of heavy metals. Many methods were used to remove lanthanides from wastewaters generated from their commercial use. Samarium, a REE, which may be removed from the aqueous solution by polyelectrolyte-enhanced ultrafiltration process, was investigated using poly(acrylic acid) (PAA) with average molecular weight 100,000 Da. The ultrafiltration studies were carried out using a tangential cell system. Polyethersulfone membrane with molecular weight cutoff of 5,000 Da and an effective filtration area of 50 cm^2 were used (PES-5). Several parameters, such as transmembrane pressure, PAA concentrations, and pH, have been optimized to improve the retention of the Sm(III**)** ions. Results shows that the permeate flux increases linearly with increasing transmembrane pressure. It can be seen that with the increase in the concentration of PAA, the Sm(III) ions retention also increases until reaching 80%. A better retention was observed at 2×10^{-4} mol L^{-1} PAA concentration and 3 bar transmembrane pressure. The pH effect study on samarium ions revealed a maximum retention around 70% for pH 5.

Keywords: Samarium (III) ions; Poly(acrylic acid) (PAA); Retention; Polyelectrolyte-enhanced ultrafiltration

1. Introduction

Rare earth elements (REEs) or lanthanides have been increasingly used in the field of chemical engineering, metallurgy, luminescence, nuclear energy, high-temperature superconductors, and catalysis among others [1]. In the past 20 years, REE turned out to be the promising elements due to their excellent properties for fine chemistry modern industry. Therefore, environmental contamination from the widespread use of REE is likely to increase [2]. However, some toxicological studies [3,4], following the recent

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employment of hi-tech materials in the electronic and semiconductor industry, have suggested that REE have significant pathogenic potential.

Lanthanides can be separated by the conventional solvent extraction technique which is usually applied to carry out the separation of metal ions [5]. Many authors used chromatography and supported liquid membranes to effect the separation of lanthanides [6,7]. These methods are not amenable to large-scale treatment of contaminated groundwater or drinking water. However, some of them have the disadvantages of using heterogeneous reactions or distribution of substances among different phases, which are the phenomena controlled by diffusion, requiring usually large operating times [8,9]. Moreover, they are often inadequate to possess high power or chemical consumption, generate sludge or solid waste, etc. [10].

The efficient and selective separation of lanthanides can be achieved by using water-soluble macroligands in combination with membrane filtration [11]. The use of membrane separation processes in the treatment of wastewater containing toxic metal ions is today an attractive and suitable technique and is easily included in the whole process [12]. For this reason, membrane separations are being employed more and more frequently. Moreover, the separation can be performed at room temperature; the modular membrane surface can be easily adjusted to the wastewater flow, and various industrial membranes are now available. In order to retain metallic ions, reverse osmosis (or at least nanofiltration) can be used due to the size of the ions in aqueous solutions. However, the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure, which makes the process expensive [13].

Therefore, efficient separation techniques which may reduce the concentration of REE to low values and achieve recovery of REE must be found. Among many separation techniques of metals from water, polymer-enhanced ultrafiltration (PEUF) process has been shown to be promising for the removal of trace metals from aqueous streams by the addition of water-soluble polymers in the wastewaters [14–20]. Since the complexation of metal ions with polymers takes place in a homogeneous phase, problems encountered with multi-phase separation are not observed. Other advantages of this method are the low energy requirements involved in the process, and the high removal efficiency due to effective binding [21]. This binding filtration process can be applied to various purposes such as treatment of waste effluents, groundwater, and surface waters.

To increase the ion rejection, the UF process can be associated with a preliminary selective complexation step of the target ions with water-soluble ligands. Thus, the resulting complexes could be rejected by the membrane, whereas the non-complexed ions pass through it. It is this principle of ultrafiltration assisted by complexation [22–26], which was applied throughout this study.

In this study, using a resistance in series model, quantification of membrane resistance, adsorption, and concentration polarization during ultrafiltration was attempted. The various filtration resistances were calculated in order to determine the principal mechanism for UF processes. The concentration polarization was observed to make the highest contribution to flux decline in the case of UF membrane.

The removal of samarium from the aqueous solutions by PEUF using the poly(acrylic acid) was investigated. The effects of transmembrane pressure, polyelectrolyte concentrations, and pH on the process efficiency, related to permeate fluxes and the retention of Sm(III) ions, are investigated in this paper.

2. Materials and methods

2.1. Reagent

The chemical reagents used in the experiments were poly(acrylic acid) (PAA) with an average molecular weight of 100,000 Da (Sigma-Aldrich), and samarium oxide (Sm_2O_3)(Ventron 99.9%), sodium hydroxide, and chloride acid used for pH adjustments and other inorganic chemicals (NaCl, Na_2SO_4) were provided by Sigma-Aldrich. All the chemicals were of analytical grade. Solutions were prepared with ultrapure water produced by Milli-Q gradient unit (Millipore).

2.2. Experimental set-up and procedure

Ultrafiltration experiments were carried out with a tangential cell system (Millipore Labscale TFF), the inlet flux was held constant (up to 0.5 m s^{-1}), and a transmembrane pressure was varied from 1 to 4 bar by restricting the outlet tube polyethersulfone membrane (PES) with molecular weight cutoff of 5,000 Da, and an effective filtration area of 50 cm^2 was used (PTGC OMS 5, Millipore). By totally recycling the permeate and the retentate, a steady state with respect to permeate quality is reached after less than half an hour under suitable temperature and pressure conditions. The presented data were collected under the steady state conditions. The temperature of the feed solution was held constant (25°C).

A schematic of the experimental ultrafiltration system is shown in Fig. 1.

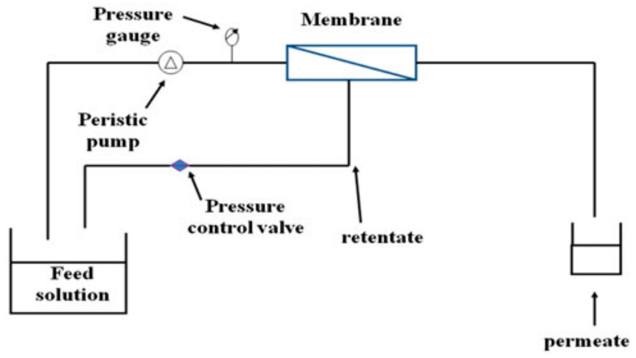

Fig. 1. Experimental ultrafiltration.

Permeate flux was calculated using the following Eq. (1):

$$J_v = \frac{V_P}{S_t} \times 100 \qquad (1)$$

where J_v is the permeate flux (L h^{-1} m^{-2}), V_p is the volume of permeate, S is effective membrane area, and t is time.

To evaluate the filtration efficiency in removing the samarium ions from the feed solution, we have used the observed retention defined as Eq. (2):

$$R = \left(1 - \frac{C_P}{C_f}\right) \times 100 \qquad (2)$$

where C_p and C_f are concentrations of solute in the permeate and feed, respectively.

After each experiment, membrane was conditioned by totally recycling ultrapure water as the permeate and the retentate. This procedure was followed by the measurement of pure water membrane permeability to ensure that initial membrane L_p^0 is restored. The L_p^0 was considered to be a reference to evaluate cleaning procedure, concentration polarization, and fouling of the membrane.

2.3. Analytical methods

Permeate samples were analyzed to determine samarium concentrations using flame atomic absorption spectrophotometry (FAAS) by the use of the Analytical Jena AAS vario 6 atomic absorption spectrophotometer. Measurements were made for each sample, by direct aspiration into protoxide of nitrogen flame of the instrument. The instrument was instructed to give the mean value and standard deviations of three readings as the final reading of each sample. pH meter (Metrohm 654), equipped with a glass electrode, was used for measuring pH solutions.

2.4. Theoretical background

The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's Law defined by Eq. (3):

$$J_w = L_p^0 \Delta P = \frac{\Delta P}{\eta^0 \times R_m} \qquad (3)$$

J_w is permeate flux of pure water (L h^{-1} m^{-2}), L_p^0 is the permeability of solvent. It depends on the solvent viscosity (η^0), and morphologic characteristics of membrane (porosity, specific surface, etc.). ΔP is the transmembrane pressure, and R_m the hydraulic membrane resistance.

According to resistance in series model, the flux decline is due to the combined effects of irreversible membrane fouling and reversible fouling (concentration polarization) over the membrane surface in addition to the membrane resistance. The hydraulic filtration resistances during UF were determined as described below [27,28].

The total resistance during ultrafiltration was determined by Eq. (4):

$$R_{tot} = \frac{\Delta P}{\eta \, J_V} \qquad (4)$$

$$R_{tot} = R_m + R_f + R_{cp} = \frac{\Delta P - \sigma \Delta \Pi}{\eta \, J_V} \qquad (5)$$

where η the dynamic viscosity of permeate (Pa s), R_m the intrinsic membrane resistance (m^{-1}), R_f the fouling layer resistance caused by internal pore clogging (m^{-1}), and R_{cp} the polarization layer resistance caused by the accumulation and deposition of polymers at the membrane surface (m^{-1}) [29].

The calculation of R_m, R_f, and R_{cp} values can be made using the above three equations and flux data.

3. Results and discussion

3.1. Ultrafiltration of samarium solution

Fig. 2a represents the variation in samarium retention as a function of the transmembrane pressure for a feed samarium concentration equal to 10^{-4} mol L^{-1}. It shows that the samarium rejection in water remained nearly constant at the value of 12%. In order to

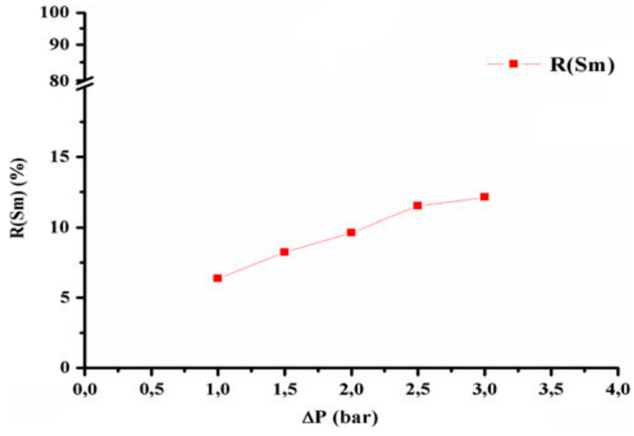

Fig .2a Samarium retention as a function of transmembrane pressure, $[Sm^{3+}]$=10-4 mol L^{-1}.

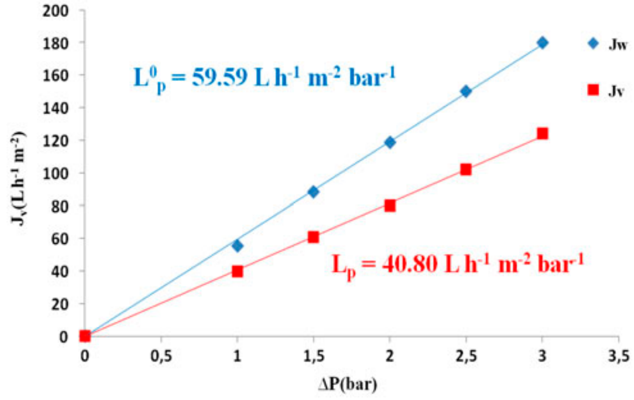

Fig. 2b Permeates fluxes of pure water and aqueous samarium solution as a function of transmembrane pressure.

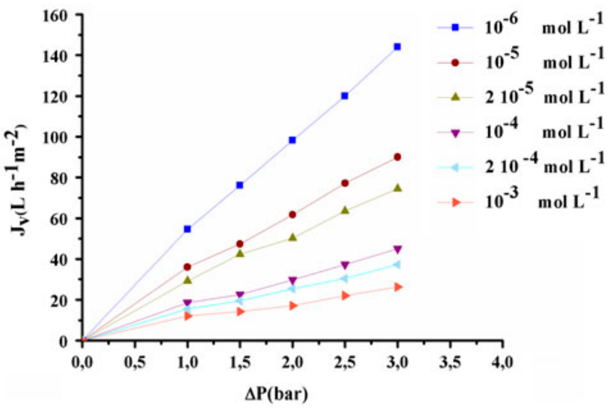

Fig. 3. Permeate flux as a function of transmembrane pressure for different PAA feed concentrations.

ameliorate this rejection, PEUF process is suitable to remove samarium ions from aqueous solutions with the help of water-soluble polymeric ligand PAA.

Pure water permeate flux (J_w) and samarium ions permeate flux (J_v) as a function of transmembrane pressure ΔP are shown in Fig. 2b. Pure solvent flux is proportional to transmembrane pressure, as it could be predicted by Eq. (3). The slopes of the straight lines are the pure water membrane permeability ($L_p^0 = 59.59$ L h^{-1} m^{-2} bar^{-1}) and samarium ions permeability ($L_p = 40.80$ L h^{-1} m^{-2} bar^{-1}).

The resulting membrane resistance and a total resistance have values 6.26×10^{12} m^{-1} and 12.53×10^{12} m^{-1}, respectively. It implies that the presence of samarium ions does not generate some significant additive resistance, generally manifested when solutes were filtered through the membrane.

3.2. Ultrafiltration of PAA solution

In Fig. 3 is displayed the variation in permeate flux as a function of the transmembrane pressure for different PAA concentrations. It shows that the permeate fluxes increases with transmembrane pressure and decreases with the increase of PAA concentrations.

The curves shown in Fig. 3 are line segments passing through the origin reflecting the negligible effect of the osmotic pressure and negligible concentration polarization. A deviation from the straight line representing J_v vs. ΔP for different PAA concentrations studied compared to pure water line.

In Table 1 are reported the experimental measurements of permeability and resistances to the solvent transfer of PAA solutions in the absence of samarium ions. It reveals a reduction in the permeability followed by an increase in total hydraulic resistance, when PAA concentrations increases from 10^{-6} to 10^{-3} mol L^{-1}. It is also noticed that total resistance increases until it reaches 10 times values higher than the intrinsic hydraulic membrane resistance. As it is well known that the flux decline is caused by several factors (concentration polarization, fouling, gel layer formation, and increase in solvent viscosity), and taking into account the observed results and lower concentrations of polyelectrolyte, fouling phenomenon is almost attributed to the resistance increase.

Indeed, the resistance due to clogging represented more than 80% of the total resistance in the case of PAA concentration is greater than 10^{-4} mol L^{-1}, and 50% in the case of PAA concentration is lower than 10^{-4} mol L^{-1}.

Table 1
Experimental measurements of permeability and resistances to the solvent transfer as a function of PAA concentrations (Δp = 3 bar)

[PAA] (mol L^{-1})	L_p (L h^{-1} m^{-2} bar^{-1})	r^2	R_{tot} (m^{-1})	R_f (m^{-1})	R_m/R_{tot} (%)	R_f/R_{tot} (%)
10^{-6}	48.75	0.996	1.25×10^{13}	6.26×10^{12}	50	50
10^{-5}	30.81	0.993	1.39×10^{13}	7.65×10^{12}	45	55
$2\ 10^{-5}$	25.57	0.990	1.79×10^{13}	1.16×10^{13}	35	64.97
10^{-4}	15.09	0.990	3.13×10^{13}	2.50×10^{13}	20	79.98
$2\ 10^{-4}$	12.59	0.987	4.17×10^{13}	3.55×10^{13}	15	84.98
10^{-3}	8.97	0.972	6.26×10^{13}	5.63×10^{13}	10	89.99

Note: R_{tot} and R_f are determined at 3 bar transmembrane pressure.

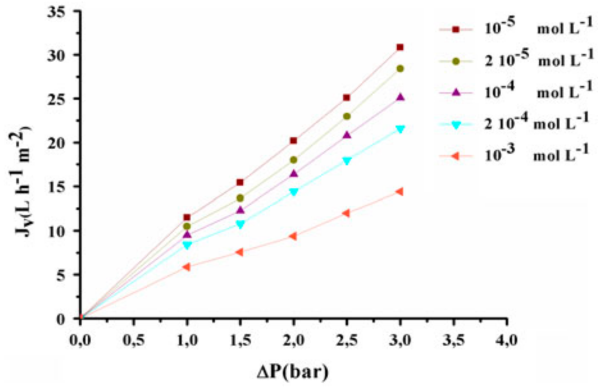

Fig. 4. Permeate flux as a function of transmembrane pressure at different PAA concentrations in the presence of samarium solution, [Sm^{3+}] = 10^{-4} mol L^{-1}.

3.3. Effect of transmembrane pressure

The variation of the permeate flux according to the transmembrane pressure at different PAA concentrations, with the presence of Sm(III) ions at 10^{-4} mol L^{-} is represented in Fig. 4.

The permeate flux increases with transmembrane pressure and decreases when PAA concentrations increases from 10^{-5} to 10^{-3} mol L^{-1}.

This reduction in permeate flux may be due to the fouling concentration polarization, gel layer formation, and increase in solvent viscosity. The increase in the osmotic pressure difference across the membrane reduces the effective transmembrane pressure and consequently decreases the permeate flux [30]. This behavior can be explained by the fact that ultrafiltration membranes are permeable to water and salt but not to polyelectrolyte molecules. And then, due to the unequal ion distribution, osmotic and swelling pressures between the two phases exist [31]. Consequently, an additional resistance to flux through membrane is observed and some membrane properties are modified (for example permeability, hydrophobic/hydrophilic relation, roughness, and pore size distribution).

In fact, experimental measurements of permeability and resistances to the transfer of the solvent in samarium–PAA mixtures are shown in Table 2. It can be observed that L_p decreases with increasing PAA concentrations. The total hydraulic resistances for ultrafiltration of PAA–samarium mixture are two times values higher than when PAA is alone (see Table 1). This can be explained by the difference of molecular weight between PAA–Sm(III) and PAA. In fact, the increase in the molecular weight of PAA, after complexing samarium ions, produces a decrease in the polyelectrolyte mobility, leading to a reduction in the diffusion from the membrane to the feed solution. On the other hand, it was thought that the overlapping of

Table 2
Experimental measurements of permeability and resistances to the transfer of the solvent in samarium–PAA (Δp = 3 bar)

[PAA] (mol L^{-1})	L_p (L h^{-1} m^{-2} bar^{-1})	r^2	R_{tot} (m^{-1})	R_f (m^{-1})	R_{cp} (m^{-1})	R_m/R_{tot} (%)	R_f/R_{tot} (%)	R_{cp}/R_{tot} (%)
10^{-5}	10.23	0.996	3.13×10^{13}	2.50×10^{13}	0	20	79.98	0
2×10^{-5}	9.32	0.995	4.17×10^{13}	3.40×10^{13}	1.50×10^{12}	15	81.39	3.6
10^{-4}	8.35	0.996	6.26×10^{13}	5.20×10^{13}	4.38×10^{12}	10	83	6.99
2×10^{-4}	7.25	0.995	8.35×10^{13}	7.10×10^{13}	6.27×10^{12}	7.5	84.98	7.51
10^{-3}	4.85	0.990	1.25×10^{14}	1.09×10^{14}	110^{13}	4.99	86.99	8.012

Note: R_{tot} and R_{cp} are determined at 3 bar transmembrane pressure.

polymer chains at the membrane surface would cause an exponential augmentation in filtration resistance.

This result shows that PES-5 membrane is more sensitive to clogging, especially for high PAA concentrations, where resistance due to clogging exceeded 80%. However, we also note that the concentration polarization phenomenon is much less important than the reversible plugging. This result shows that the importance for step washing and cleaning membranes allow us to eliminate the majority of clogging particles.

On the other hand, the variation of samarium rejection as a function of transmembrane pressure for different PAA concentrations with the presence of Sm(III) ions at 10^{-4} mol L^{-1} is represented in Fig. 5. It shows that samarium retention increases with the increase in PAA concentrations from 10^{-5} to 2×10^{-4} mol L^{-1}, until reaching 80%. Beyond 2×10^{-4} mol L^{-1} PAA concentration, retention of samarium decreases. This is mainly attributed to several phenomena, such as concentration polarization, membrane fouling, osmotic pressure, precipitation, and formation of a gel layer on the membrane surface [32].

The analysis of both figures calls for caution not to exceed 3 bar in transmembrane pressure; otherwise, samarium ions retention would be endangered and concentration polarization would be enhanced. A best retention was observed at 2×10^{-4} mol L^{-1} PAA concentrations.

3.4. pH effect

In order to determine the effect of pH on samarium ions retention efficiency, the experiments were performed with fixed samarium ions concentration of 10^{-4} mol L^{-1}, PAA concentration of 2×10^{-4} mol L^{-1}, and transmembrane pressure of 3 bar under varied pH solutions.

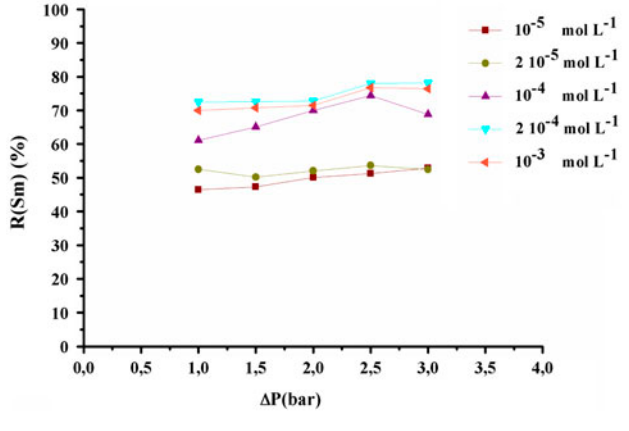

Fig. 5. Samarium retention as a function of transmembrane pressure at different PAA concentrations, $[Sm^{3+}] = 10^{-4}$ mol L^{-1}.

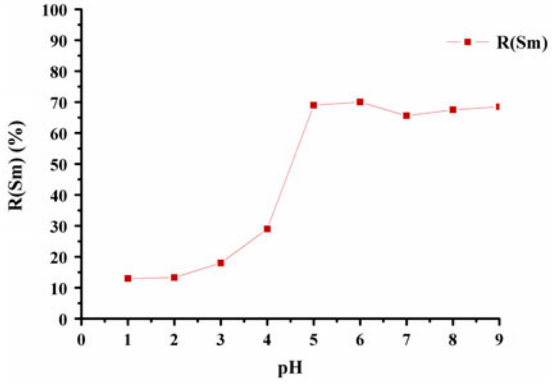

Fig. 6a. Samarium retention as a function of the feed pH, $[Sm^{3+}] = 10^{-4}$ mol L^{-1}, [PAA] = 2.10^{-4} mol L^{-1}, and ΔP = 3 bar.

Fig. 6a shows the variation samarium retention as a function of pH. It show that retention increases with the rise of pH to reach 70% at pH 5. The increase in pH leads to an increase in deprotoned carboxylic groups concentration, which favors the formation of macromolecular PAA–Sm complexes, and subsequently an increase in metal rejection coefficients [33]. The membrane charge varies with the pH around its isoelectric point. At pH beyond isoelectric point, the membrane is negatively charged. Associated with a pH solution, carboxylic groups of polymer start dissociating and the presence of carboxylate anions (COO^{-}) becomes more important. The electrical charges existing in the molecules lead to the apparition of intramolecular and intermolecular repulsion forces.

On the other hand, Fig. 6b describes permeate flux as a function of initial pH. This figure shows the effect

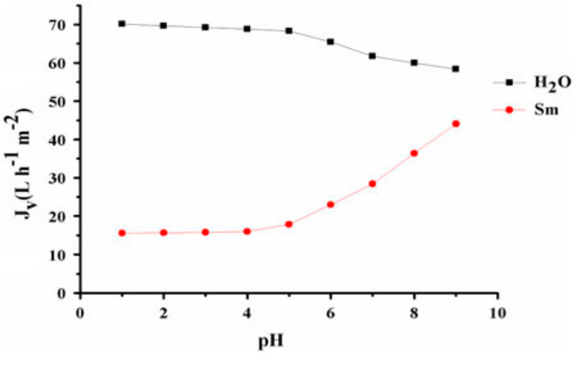

Fig. 6b. Permeate fluxes of water, Sm(III) as a function of the feed pH $[Sm^{3+}] = 10^{-4}$ mol L^{-1}, [PAA] = 2×10^{-4} mol L^{-1}, and ΔP = 3 bar.

of pH on permeate flux, with values fluctuating around 15–55% of the pure water flux. In fact, increase in pH provokes molecule expansion, which increases slightly the viscosity of polymer solutions. However, permeate fluxes increase until pH 5, which means that rod-like structure of polymer and high turbulence imposed by the presence of internal rod minimize partially the membrane fouling. When pH of solution grows, permeate fluxes increases, and it can be explained by the massive presence of carboxylate groups that facilitate the interaction between polymer and membrane [34].

It can be also observed that permeate flux increases as far as pH increases. In fact, this behavior can be explained on the basis of conformational changes of polymer structure and interactions between polymer molecules themselves and membrane.

Since the ionization degree of carboxylic groups is low at low pH values, the charge repulsion between polyelectrolyte and membrane diminishes and then, the polymer sorption efficiency rises [35].

4. Conclusions

In this paper, enhanced ultrafiltration by the addition poly(acrylic acid) with average molecular weight 100,000 Da, for the removal of samarium ions from aqueous solutions, has been studied.

The resistance in series model was followed, and membrane resistance, adsorption, and concentration polarization during ultrafiltration were quantified.

The various filtration resistances (R_m, R_f and R_{cp}) were calculated in order to determine the principal mechanism for UF processes. The concentration polarization was observed to make the highest contribution to flux decline. The UF membrane showed that the fouling had an important contribution to flux decline which was principally generated by reversible fouling.

The variation in permeate flux as a function of the transmembrane pressure for different PAA concentrations was studied. It showed that the permeate flux increases with transmembrane pressure and decreases with the increase of PAA concentration. This reduction may be due to the fouling concentration polarization, gel layer formation, and increase in solvent viscosity.

Samarium retention also increases until reaching 80%. A better retention was observed at 2×10^{-4} mol L^{-1} PAA concentration and 3 bar transmembrane pressure.

The pH effect study on samarium ions recovery revealed a maximum retention around 70%, for pH 5. It can be also observed that permeate fluxes increases with increasing pH. These results can be explained by a conformational change on the polymer chains, a competitive adsorption between H^+ and (Sm^{3+}) on negatively charged polymer and the attenuation of the electrostatic repulsion.

List of symbols

REE — rare earth elements
PEUF — polyelectrolyte-enhanced ultrafiltration
PAA — poly(acrylic acid)
Da — Dalton
MWCO — molecular weight cutoff
PES-5 — polyethersulfone membrane with (MWCO) of 5,000 Da
Sm(III) — samarium (III)
UF — ultrafiltration
J_v — permeate flux (L h^{-1} m^{-2})
V_p — volume of permeate (mL)
S — effective membrane area (cm^2)
t — time (s)
R — retention of samarium (III) (%)
C_p — concentration of solute in the permeate (mol L^{-1})
C_f — concentration of solute in the feed solution (mol L^{-1})
FAAS — flame atomic absorption spectrophotometry
AAS — atomic absorption spectrophotometer
J_w — permeate flux of pure water (l h^{-1} m^{-2})
L_p^0 — permeability of solvent (l h^{-1} m^{-2} bar^{-1})
η^0 — viscosity of solvent
ΔP — transmembrane pressure (bar)
R_m — hydraulic membrane resistance (m^{-1})
η — dynamic viscosity of permeate (pa s)
R_{tot} — total resistance
R_f — fouling layer resistance (m^{-1})
R_{cp} — polarization layer resistance (m^{-1})
L_p — permeability of samarium ions (l h^{-1} m^{-2} bar^{-1})
[PAA] — concentration of poly(acrylic acid)
[Sm^{3+}] — concentration of samarium

References

[1] P. Maestro, D. Huguenin, Industrial applications of rare earths: Which way for the end of the century, J. Alloys Compd. 225 (1995) 520–528.

[2] R. Filipi, K. Nesmerak, M. Rucki, Z. Roth, I. Hanzlikova, M. Tichy, Acute toxicity of rare earth elements and their compounds, Chem. Listy 101 (2007) 793–798.

[3] P.J. Haley, Pulmonary toxicity of stable and radioactive lanthanide, Health Phys. 61 (1991) 809–820.

[4] S. Hirano, K.T. Suzuki, Exposure, metabolism and toxicity of rare earths and related compounds, Environ. Health Perspect. 104 (1996) 85–95.

[5] M. Yamaguchi, Extractive separation of praseodymium and neodymium by di(2-ethylhexyl) phosphoric acid in the presence of water-soluble complexing agents using an electrostatic liquid-liquid contactor, Chem. Eng. Res. Des. 75 (1997) 447–452.

[6] D.O. Campbell, S.R. Buxton, Rapid ion exchange separations. Chromategraphic lanthanide separations using a high-pressure ion exchange method, Ind. Eng. Chem. Process Des. Dev. 9 (1970) 89–94.

[7] M. Carlos, H. Aleš, V. Manuel, Permeation of neodymium and praseodymium through supported liquid membranes containing di-(2-ethylhexyl) phosphoric acid as a carrier, J. Membr. Sci. 81 (1993) 121–126.

[8] C. Abbruzzese, P. Fornari, R. Massidda, T.S. Urbanski, Solvent extraction of lanthanum (III) and cerium (III) from aqueous chloride solutions by LIX 70, Hydrometallurgy 28 (1992) 179–190.

[9] J. Ludek, Y. Wei, K. Mikio, Adsorption of Ce(IV) anionic nitrato complexes onto anion exchangers and its application for Ce(IV) separation from Rare Earths(III), J. Rare Earths 24 (2006) 385–391.

[10] R.D. Abreu, C.A. Morais, Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide, Miner. Eng. 23 (2010) 536–540.

[11] M.V. Norton, F.A. DiGiano, R.T. Hallen, Selective separation of europium using polymer-enhanced ultrafiltration, Water Environ. Res. 69 (1997) 244–253.

[12] R. Molinari, S. Gallo, P. Argurio, Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation, Water Res. 38 (2004) 593–600.

[13] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[14] R.S. Juang, R.C. Shiau, Metal removal from aqueous solutions using chitosan-enhanced membrane filtration, J. Membr. Sci. 165 (2000) 159–167.

[15] N. Fatin-Rouge, A. Dupont, A. Vidonne, J. Dejeu, P. Fievet, A. Foissy, Removal of some divalent cations from water by membrane-filtration assisted with alginate, Water Res. 40 (2006) 1303–1309.

[16] M. Bodzek, I. Korus, K. Loska, Application of the hybrid complexation–ultrafiltration process for removal of metal ions from galvanic wastewater, Desalination 121 (1999) 117–121.

[17] R. Molinari, P. Argurio, T. Poerio, Comparison of polyethylenimine, polyacrylic acid and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) in Cu^{2+} removal from wastewaters by polymer-assisted ultrafiltration, Desalination 162 (2004) 217–228.

[18] R. Molinari, S. Gallo, P. Argurio, Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation, Water Res. 38 (2004) 593–600.

[19] C. Dilek, H.O. Ozbelge, N. Bicak, L. Yilmaz, Removal of boron from aqueous solutions by continuous polymer-enhanced ultrafiltration with polyvinyl alcohol, Sep. Sci. Technol. 37 (2002) 1257–1271.

[20] Y.F. Zhang, Z.L. Xu, Study on the treatment of industrial wastewater containing Pb^{2+} ion using a coupling process of polymer complexation–ultrafiltration, Sep. Sci. Technol. 37(7) (2003) 1585–1596.

[21] A. Rether, M. Schuster, Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers, React. Funct. Polym. 57 (2003) 13–21.

[22] D.J. Ennigrou, L. Gzara, M.R.B. Romdhane, M. Dhahbi, Retention of cadmium ions from aqueous solutions by poly(ammonium acrylate) enhanced ultrafiltration, Chem. Eng. J. 155 (2009) 138–143.

[23] R. Camarillo, J. Llanos, L. García-Fernández, Á. Pérez, P. Canizares, Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction, Sep. Purif. Technol. 70 (2010) 320–328.

[24] J. Zeng, H. Ye, Z. Hu, Selective separation of Hg(II) and Cd(II) from aqueous solutions by complexation–ultrafiltration process, J. Hazard. Mater. 161 (2009) 1491–1496.

[25] D. Zamariotto, B. Lakard, P. Fievet, N. Fatin-Rouge, Retention of Cu(II)– and Ni(II)–polyaminocarboxylate complexes by ultrafiltration assisted with polyamines, Desalination 258 (2010) 87–92.

[26] Y.R. Qiu, L.J. Mao, Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid, Desalination 329 (2013) 78–85.

[27] P. Rai, C. Rai, G.C. Majumdar, S. DasGupta, S. De, Resistance in series model for ultrafiltration of mosambi (*Citrus sinensis* (L.) Osbeck) juice in a stirred continuous mode, J. Membr. Sci. 283 (2006) 116–122.

[28] T.S. Pathak, K.Y. Chung, Surface modification and permeation characteristics of PVDF membrane after graft polymerization using polar monomer, J. Ind. Eng. Chem. 12 (2006) 539–545.

[29] X. Zhu, K.H. Choo, A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane, Colloids Surf., A 312 (2008) 231–237.

[30] S.K. Karode, A method for prediction of the gel layer concentration in macromolecular ultrafiltration, J. Membr. Sci. 171 (2000) 131–139.

[31] W.R. Bowen, P.M. Williams, Quantitative predictive modelling of ultrafiltration processes: Colloidal science approaches, J. Colloid Interface Sci. 134–135 (2007) 3–14.

[32] S. De, P.K. Bhattacharya, Modeling of ultrafiltration process for a two component aqueous solution of low and high (gel-forming) molecular weight solutes, J. Membr. Sci. 136 (1997) 57–69.

[33] I.M. Villoslada, E. Quiroz, C. Munoz, B.L. Rivas, Use of ultrafiltration on the analysis of low molecular weight complexing molecules. Analysis of iminodiacetic acid at constant ionic strength, Anal. Chem. 73 (2001) 5468–5471.

[34] S. Chibowski, M. Wiśniewska, A.W. Marczewski, S. Pikus, Application of the SAXS method and viscometry for determination of the thickness of adsorbed polymer layers at the ZrO_2–polymer solution interface, Colloid Interface Sci. 267 (2003) 1–8.

[35] B. Bednar, J. Trnena, P. Svoboda, S. Vajda, V.K. Fidler, K. Prochazka, Time-resolved fluorescence study of chain dynamics. 1. Poly(methacrylic acid) in dilute water solutions, Macromolecules 24 (1991) 2054–2059.