Retention of cadmium ions from aqueous solutions by poly(ammonium acrylate) enhanced ultrafiltration

Dorra Jellouli Ennigrou, Lassaad Gzara, Mohamed Ramzi Ben Romdhane, Mahmoud Dhahbi*

Laboratoire Eau et Technologies Membranaires, BP 273, 8020 Soliman, Tunisia

ARTICLE INFO

ABSTRACT

Cadmium removal from aqueous solution by polyelectrolyte enhanced ultrafiltration (PEUF) with relatively low transmembrane pressure was investigated at varying conditions of polyelectrolyte and cadmium concentrations, transmembrane pressure, ionic strength and pH. The poly(ammonium acrylate), with two average molecular weights (8000 and 15 000 Da) were used as polyelectrolyte. Flux declines during ultrafiltration of polyelectrolyte solutions. An effort has been made to evaluate these resistances independently at different operating conditions. The hydraulic membrane resistance is higher for processing solutions of $PAmA_8$ than solutions of $PAmA_{15}$. The study of ionic strength effect demonstrates that it decreases the retention of cadmium ions and increases the permeate flux. More than 99% of cadmium was retained for a $NaNO_3$ feed concentration less than 5×10^{-2} mol L^{-1}. The pH effect study on the cadmium recovery revealed a maximum retention around 98% for pH 4.

1. Introduction

The continuous increase of world needs for the most of the known metals, the decrease in grade of the available ores, and strict environmental regulations, make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations [1].

The use of membrane separation process in treating wastewater containing toxic metal ions is today an attractive and suitable technique, and it has to be easily included in whole process, which is the reason why membrane separations are being used more and more frequently. On the other hand, separation can be carried at room temperature; the modular membrane surface can be easily adjusted to the wastewater flows; 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. But the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure, which makes the process expensive [2].

Among the membrane methods, there are two widely used separation techniques for the removal of heavy metal ions from aqueous solutions: micellar enhanced ultrafiltration (MEUF) and polyelectrolyte ultrafiltration. MEUF [3–8] and PEUF [9–19] combine ultrafiltration with the presence of water-soluble surfactants and polymers, respectively. The enhanced ultrafiltration processes have advantage of operating at relatively low pressures and temperatures resulting in excellent rejection of multivalent metals and organics.

PEUF is the combination of two phenomena, binding of metal ions to a water-soluble natural or synthetic polyelectrolyte, and ultrafiltration. Since pore size of ultrafiltration membranes are not suitable to separate heavy metal ions, water-soluble polymers are used to bind the metals to form macromolecular complexes rejected by ultrafiltration.

The majority of PEUF studies reported to date have focused mainly on demonstrating the effectiveness of the process on metal removal under various experimental conditions such as solution pH, metal loading ratio, the types of polyelectrolytes and metals, and the molecular weight cut-off (MWCO) and types of membranes.

Flux decline with time of operation is the major problem in UF [3,10]. In most of the industrial applications, the flux decline during the UF is the cumulative effect of several mechanisms including adsorption of solutes on the membrane surface, pore plugging, concentration polarization, etc.

In the present study, using a resistance-in-series model, quantification of membrane resistance, adsorption and concentration polarization during filtration was attempted. An effort has been made to evaluate these resistances independently at different operating conditions. The removal of cadmium from aqueous solutions by PEUF using the poly(ammonium acrylate) was investigated as function of some parameters such as ionic strength, pH, concentration and the molecular weights of polyelectrolyte.

---

2. Materials and methods

2.1. Reagents

A poly(ammonium acrylate) produced by radical polymerisation of ammonium acrylate monomer in aqueous medium at 60 °C during 2 h with potassium persulfate ($K_2S_2O_8$) as initiator and sodium metabisulfite ($K_2S_2O_5$) as activator. After precipitation in acetone, the copolymer was isolated, dried under a nitrogen atmosphere, then dissolved in water to provide a concentrated solution.

$$-(CH_2—CH)_n$$
$$COO^-NH_4^+$$

PAmA
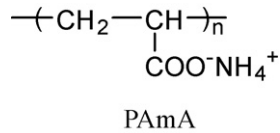
The measurement of the intrinsic viscosity [η] permits to estimate the viscosimetric average molecular weight (M_w) of the two polyelectrolytes synthesized, this viscosity is determined by Mark–Houwink relation [20]

$$[\eta] = K M_w^a \tag{1}$$

where [η] is the intrinsic viscosity in dl g^{-1}.

K and a are constants depending on the nature of the polymer and of the solvent. In our case

$$M_w = \left(\frac{\eta}{3.75 \times 10^{-4}} \right)^{1/0.7} \tag{2}$$

Intrinsic viscosity was measured in KCl solution (1 mol L^{-1}) using a Ubbelhode viscosimeter.

Ubbelhode capillary viscosimeter was used in this study. It is operated by filling it with a suitable volume of liquid, drawing the liquid level to the upper mark above the bulb, and measuring the time required for the liquid meniscus to fall from the upper mark to the lower mark. The viscosity is proportional to the flow time.

The results are summarized in Table 1.

Cadmium chloride (CdCl$_2$·2H$_2$O), sodium hydroxide, nitric acid, and sodium nitrate 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. Analytical methods

Permeate samples were analyzed to determine cadmium 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 air acetylene 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.

pHmeter (Metrohm 654), equipped with a glass electrode was used for measuring pH solutions.

Table 1
Polyelectrolyte characterization.

Polymer	Supplier	Intrinsic viscosity [η] in (dl g^{-1})	Average molecular weight (M_w)
PMA-M+	Darvan C–Vanderbilt, GB	2.52	10 000[a]
PAmA$_8$	Synthesized	2.15	8000[b]
PAmA$_{15}$	Synthesized	3.35	15 000[b]

[a] Based on technical data.
[b] Determined by Eq. (2).

2.3. Experimental setup and procedure

Ultrafiltration experiments were carried out with a tangential cell system (Minitan-S, Millipore). The inlet flux was held constant (up to 0.5 m s^{-1}) and a drop in pressure was varied from 0.6 to 2 bar by restricting the outlet tube. Polysulfone membranes with molecular weight cut-off (MWCO) of 10 kDa and an effective filtration area of 30 cm^2 were used (PTGC OMS 10, 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 given temperature and pressure conditions. The data presented here were collected under steady state conditions. The temperature of the feed solution was held constant (30 °C).

Permeate flux was calculated using the following equation:

$$J_v = \frac{V_p}{St} \tag{3}$$

where V_p is the volume of permeate, S is effective membrane area and t is time.

For the comparison of the fluxes measured in different conditions to be rigorously valid, the flux with pure water was systematically checked between two experiments to ensure that there was no flux decline due to partial plugging. In case of flux decline the cleaning procedure was pursued until the reference flux was obtained, or a new membrane was used.

To evaluate the filtration efficiency in removing the cadmium ions from the feed solution, we have used the observed retention defined as:

$$R = 1 - \frac{C_{per}}{C_i} \tag{4}$$

where C_{per} and C_i are concentration of metal ions in permeate and feed, respectively.

2.4. Theoretical background

The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's Law:

$$J_{wi} = L_p \Delta P = \frac{\Delta P}{\eta R_m} \tag{5}$$

L_p 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 is 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 [21,22].

$$R_m = \frac{\Delta P}{\eta J_{wi}} \tag{6}$$

$$R_m + R_f + R_p = \frac{\Delta P - \sigma \Delta \Pi}{\eta J_v} \tag{7}$$

$$R_m + R_f = \frac{\Delta P}{\eta J_{wf}} \tag{8}$$

where J_{wi}, J_{wf}, and J_v are the fluxes (L h^{-1} m^{-2}) using pure deionized water in the initial and final stages and actual polymer solutions, respectively; ΔP is the transmembrane pressure (bar); η is the dynamic viscosity of permeate (Pa); R_m is the intrinsic membrane resistance (m^{-1}); R_p is the polarization layer resistance caused by the accumulation and deposition of polymers at the membrane surface (m^{-1}); and R_f is the fouling layer resistance caused by internal pore clogging (m^{-1}) [9].
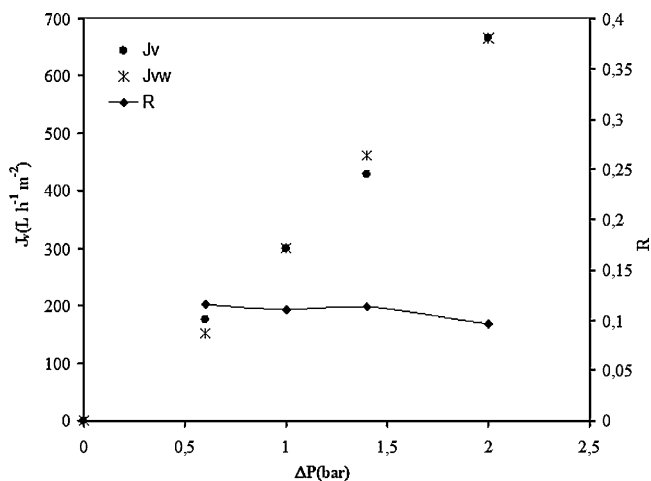
Fig. 1. Cadmium retention and permeates flux of cadmium solution as a function of transmembrane pressure at $\theta = 30\,^\circ$C and $[Cd^{2+}] = 10^{-3}$ mol L^{-1}.

The calculation of R_m, R_f, and R_p values can be made using the above three equations and flux data.

3. Results and discussion

3.1. Ultrafiltration of cadmium solution

Fig. 1 represents the variation of cadmium retention as a function of the transmembrane pressure for a feed cadmium concentration equal to 10^{-3} mol L^{-1} at 30 °C. It shows that the cadmium rejection in water remained practically constant at the value of 11%.

In Fig. 1 pure water permeate fluxes (J_{vw}) and aqueous cadmium solution permeate fluxes (J_v) are shown as a function of transmembrane pressure ΔP. First, pure solvent flux is proportional to transmembrane pressure, as it could be predicted by Eq. (5). The slopes of the straight lines are the pure water membrane permeability ($L_P^0 = 323.76$ L h^{-1} m^{-2} bar^{-1}) and aqueous cadmium solution permeability ($L_p = 319.56$ L h^{-1} m^{-2} bar^{-1}). The resulting membrane resistance and a hydraulic total resistance have as values 1.39 and 1.41×10^{12} m^{-1} respectively. It implies that the presence of cadmium ions does not generate some significant additive resistance, generally manifested when solutes where filtered through the membrane.

3.2. Ultrafiltration of PAmA solution

In Fig. 2 is displayed the variation of permeate flux as a function of the transmembrane pressure for different feed concentrations of
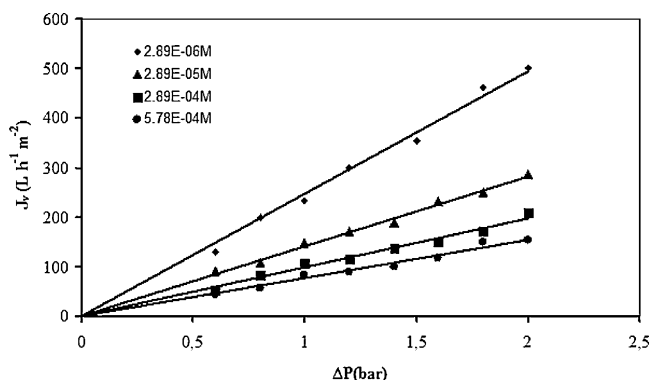

Fig. 2. Permeate flux as a function of transmembrane pressure for different PAmA$_{15}$ feed concentrations at $\theta = 30\,^\circ$C.

PAmA$_{15}$. It shows that the permeate flux increases with transmembrane pressure and decreases with the increase of polyelectrolyte concentration.

It can be seen also, from curves obeying to Darcy law ($J_{wi} = L_p \Delta P$), that in the studied range of the transmembrane pressure and polyelectrolyte concentration, insignificant polarization concentration phenomenon and negligible osmotic pressure were observed. In Table 2 are reported the experimental measurements of permeability and resistances to the solvent transfer of PAmA$_{15}$ solutions in absence of cadmium. It reveals a reduction of the permeability followed by an increase in total hydraulic resistance, when the concentration of PAmA$_{15}$ increases from 2.89×10^{-6} to 5.78×10^{-4} mol L^{-1}. It is also noticed that total resistance increases until it reaches four 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 of solvent viscosity), and taking into account the observed results and lower concentrations of polyelectrolyte, fouling phenomenon is almost attributed of the resistance increase.

3.3. Ultrafiltration of the mixture PAmA–cadmium

The variation of the permeate flux according to the transmembrane pressure at different concentrations of PAmA (15 and 8) with the presence of Cd^{2+} at 10^{-3} mol L^{-1} is represented respectively in Fig. 3(a and b). Experimental measurements of permeability, osmotic pressure and resistances to the transfer of the solvent in cadmium–PAmA (15 and 8) mixtures are given in Tables 3 and 4 respectively.

According to Fig. 3, it can be noticed that the variation of flux with the transmembrane pressure does not follow the Darcy's law, but flux varies according to Eq. (7). Obtained results indicate that ultrafiltration of mixtures of PAmA–cadmium is affected by the osmotic pressure gradient. Tables 3 and 4 show that osmotic pressure increases with increasing feed polyelectrolyte concentration. This behaviour 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 [23].

Fig. 3 also demonstrates that flux decreases with an increase of feed polyelectrolyte concentration. Nevertheless, PAmA$_{15}$ permeability values are the highest compared to PAmA$_8$. These higher values can be explained by the membrane pores plugging when PAmA$_8$ is used (the molecular weight is equal to the cut-off of the membrane). In the case of PAmA$_{15}$, the former remains at the membrane surface and will be swept under the effect of the fluid tangential circulation (the molecular weight is higher than the cut-off of the membrane). For low polyelectrolyte concentrations, i.e. 1.44 and 3.71×10^{-4} mol L^{-1} PAmA (15 and 8) concentrations, respectively, Fig. 3 shows a linear variation in the range of the studied pressure (0–2 bar). Above these concentration values, the shape of curves is similar to the shape when concentration polarization phenomenon occurs. In addition to this concentration polarization phenomenon, polymer–polymer interactions became significant at higher concentration leading to the overlapping of polymer molecules. In fact, the transition concentration of polymer solution from dilute to semi-dilute regimes, which is defined as the overlap concentration, affects the processing of the solutions and then the permeability values.

Zhu and Choo [24] have developed new simplified equation that incorporated resistance-in-series UF model into the osmosis phenomenon caused by polymers, and then applied to estimate the threshold concentration for macromolecular overlap.

Tables 3 and 4 revealed a reduction of permeability L_p followed by an increase of the total hydraulic resistance R_{tot}, when the con-

Table 2
Experimental measurements of permeability and resistances to the solvent transfer as a function of PAmA$_{15}$ concentration.

[PAmA]$_{15}$ (mol L^{-1})	L_p (L h^{-1} m^{-2} bar^{-1})	r^2	R_{tot} (m^{-1})	R_f (m^{-1})
2.89×10^{-6}	243.54	0.987	1.85×10^{12}	4.62×10^{11}
1.44×10^{-5}	142.88	0.974	3.15×10^{12}	1.76×10^{12}
2.89×10^{-5}	141.25	0.996	3.19×10^{12}	1.80×10^{12}
1.44×10^{-4}	127.80	0.984	3.52×10^{12}	2.13×10^{12}
2.89×10^{-4}	98.35	0.999	4.58×10^{12}	3.19×10^{12}
5.78×10^{-4}	76.64	0.983	5.88×10^{12}	4.49×10^{12}

Table 3
Experimental measurements of permeability, osmotic pressure and resistances to the transfer of the solvent in cadmium–PAmA$_{15}$ mixtures.

[PAmA]$_{15}$ (mol L^{-1})	L_p (L h^{-1} m^{-2} bar^{-1})	$\sigma\Delta\Pi$	R_f (m^{-1})	R_{tot} (m^{-1})	R_{CP} (m^{-1})
2.89×10^{-6}	140.93	0.031	1.85×10^{12}	3.23×10^{12}	0
1.44×10^{-5}	132.62	0.045	2.05×10^{12}	3.47×10^{12}	0
2.89×10^{-5}	129.44	0.095	2.13×10^{12}	3.53×10^{12}	0
1.44×10^{-4}	119.60	0.131	2.42×10^{12}	4.40×10^{12}	5.92×10^{11}
2.89×10^{-3}	99.40	0.151	3.19×10^{12}	5.17×10^{12}	5.80×10^{11}
5.78×10^{-3}	83.50	0.252	4.08×10^{12}	6.72×10^{12}	1.24×10^{12}

R_{tot} and R_{cp} are determined at 2 bar transmembrane pressure.

Table 4
Experimental measurements of the permeability, osmotic pressure and resistances to the transfer of the solvent in cadmium–PAmA$_8$ mixtures.

[PAmA]$_8$ (mol L^{-1})	L_p (L h^{-1} m^{-2} bar^{-1})	$\sigma\Delta\Pi$	R_f (m^{-1})	R_{tot} (m^{-1})	R_{cp} (m^{-1})
7.43×10^{-6}	135.82	0.136	1.98×10^{12}	3.62×10^{12}	0
3.71×10^{-5}	123.19	0.171	2.29×10^{12}	3.72×10^{12}	0
7.43×10^{-5}	116.77	0.211	2.50×10^{12}	3.91×10^{12}	0
3.71×10^{-4}	103.13	0.236	3.03×10^{12}	5.09×10^{12}	6.71×10^{11}
7.43×10^{-4}	90.65	0.254	3.65×10^{12}	6.20×10^{12}	1.17×10^{12}
1.48×10^{-3}	69.08	0.371	5.20×10^{12}	8.10^{12}	1.41×10^{12}

R_{tot} and R_{cp} are determined at 2 bar transmembrane pressure.

centration of PAmA increases. For higher polymer concentrations, a decline of permeate flux can be explained by gel layer formation and concentration polarization occurrence.

The total hydraulic resistances for ultrafiltration of PAmA$_{15}$–cadmium mixture were almost two times higher than PAmA$_{15}$ resistance values (see Table 2). This can be explained by the difference of molecular weight between PA–Cd^{2+} and PA–NH$_4^+$. In fact, the increase of the molecular weight of PAmA, after complexing the cadmium ions, produces a decrease of the polyelectrolyte mobility leading to a reduction of the diffusion from the membrane to the feed solution. On the other hand, it was thought that the overlapping of polymer chains at the membrane surface would cause an exponential augmentation in filtration resistance.

Considering that the background electrolytes and the types of background ions may affect the overlap concentration. Cadmium which replaces ammonium present in the negatively charged polymer chains may cause a change of the polymeric solution characteristics. In fact, the polyelectrolyte viscosity decreased and was stiffer when ammonium was replaced by cadmium [25], which may have given rise to an increase in the overlap concentration.

In Fig. 4 is displayed the variation of cadmium retention and solvent permeate flux as a function of monomer unit PAmA$_8$ and PAmA$_{15}$ concentration, respectively. It shows that, when polyelectrolyte monomers concentration rises, cadmium retention increases until reaching 99 and 95% at 2.43×10^{-3} mol L^{-1} (about 2-fold cadmium concentration) and 3.33×10^{-3} mol L^{-1} PAmA$_{15}$ and PAmA$_8$ monomer unit concentration, respectively. Above these values, retention remains higher than 99%. For acrylate moieties concentrations lower than 5×10^{-3} mol L^{-1}, observed cadmium rejection values, obtained when PAmA$_{15}$ has been used, are higher than rejection values found with PAmA$_8$, which has an average molecular weight lower than the membrane MWCO, the showed

results can be explained by the possible leakage of the PAmA$_8$ and, consequently, the adsorbed Cd(II).

Moreover and for the both cases, it can be observed that the permeate flux remained constant for a monomeric unit concentration equal to 5×10^{-3} mol L^{-1}. For higher concentrations, a flux decline was observed. Correspondingly, as demonstrated by Zhu and Choo [24], there was a linear increase in filtration resistance with low polymer concentrations, whereas with higher polymer concentrations, an exponential increase took place indicating the overlap concentration.

3.4. Effect of ionic strength

The effect of ionic strength on UF cadmium rejection and permeate fluxes is depicted in Fig. 5. This figure shows that the cadmium retention remains around 99% until 5×10^{-2} mol L^{-1} NaNO$_3$. Beyond this concentration, rejection of cadmium decreases sharply to attain 17% at 5×10^{-1} mol L^{-1} of NaNO$_3$. It shows also that permeate fluxes increase slightly (not exceeding 22%) with the increase of NaNO$_3$ concentration. These results can be explained by a conformational change on the polymer chains, a competitive adsorption between Na$^+$ and Cd^{2+} on negatively charged polymer and the attenuation of the electrostatic repulsion. It is well known that negatively charged polyelectrolytes interact with positively charged divalent metal ions stronger than with monovalent ions [26,27]. Nevertheless, the filtration of metal ions and their subsequent release from the polymer induces an increase of the net negative charge on the polymer surface and then an expansion of the chains in order to increase the total surface, minimizing the electrostatic repulsions. Related with this, the decrease on the surface charge density of the polymer induces a decrease on the strength of the interactions with the metal ions, and in consequence, their easier release to the solution from the polymer domain during filtration.
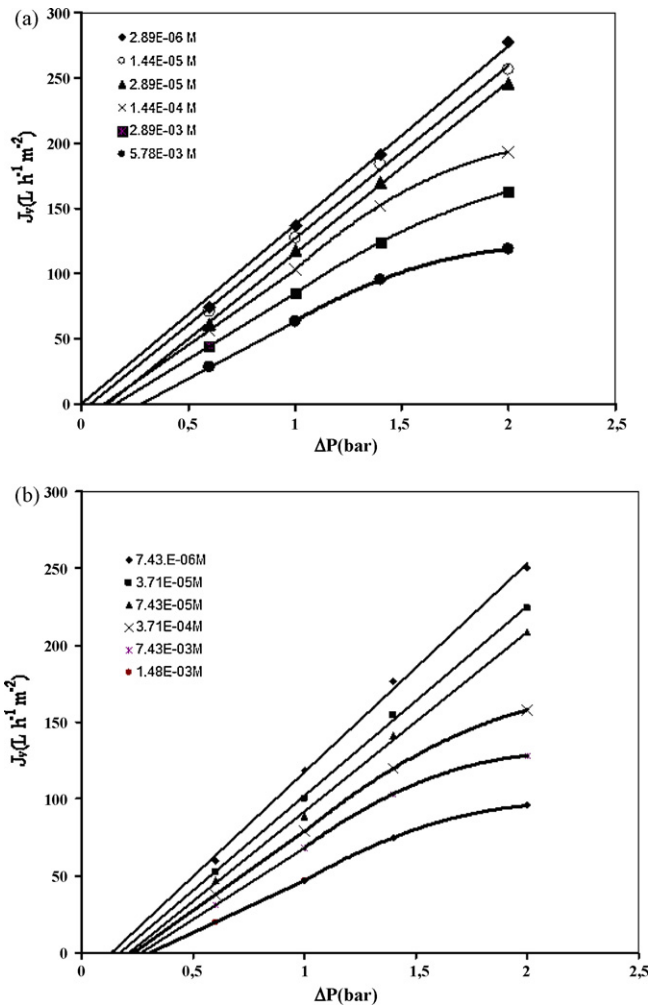
Fig. 3. Permeate flux as a function of transmembrane pressure at different PAmA concentrations in presence of initial cadmium concentration equal to 10^{-3} mol L^{-1} (a) PAmA$_{15}$ and (b) PAmA$_8$.
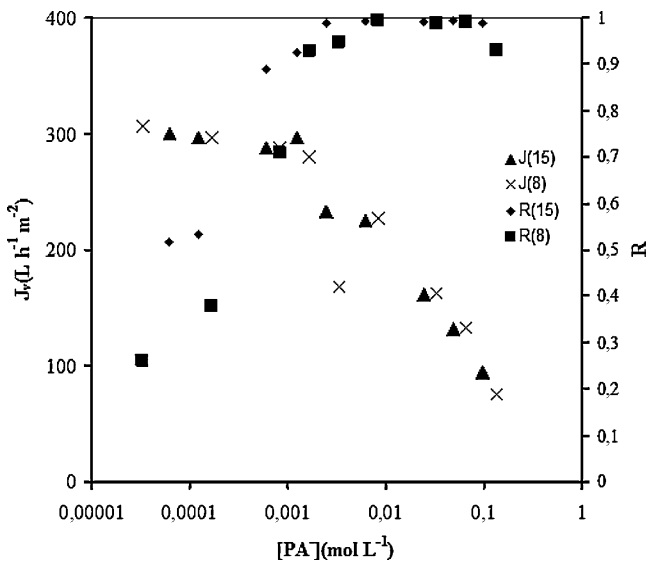

Fig. 4. Cadmium retention and permeates flux as a function of monomeric unit PAmA (8 and 15) concentration at $\theta = 30\,^{\circ}$C, pH = 6.5 and $\Delta P = 2$ bar.
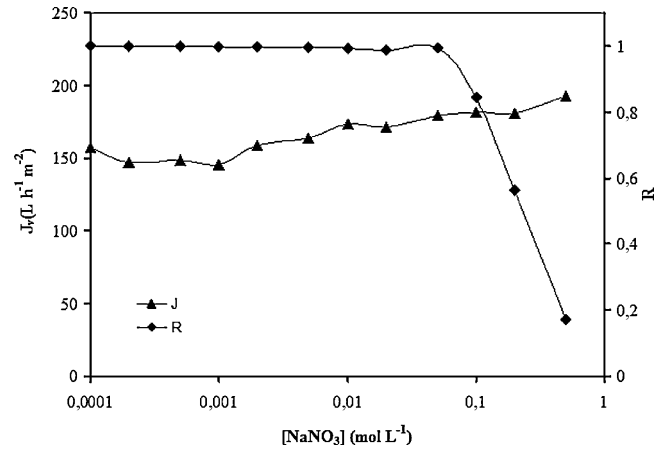

Fig. 5. Cadmium retention and permeate flux as a function of NaNO$_3$ concentration. [Cd^{2+}] = 10^{-3} mol L^{-1}, [PAmA]$_8$ = 3.71×10^{-4} mol L^{-1}, at $\theta = 30\,^{\circ}$C, pH = 6.5 and $\Delta P = 2$ bar.

3.5. pH effect

Fig. 6 depicts the influence of pH feed solution on permeate flux and cadmium retention in the presence of PAmA$_8$ at 3.71×10^{-4} mol L^{-1} (3.33×10^{-2} mol L^{-1} monomer unit concentration). The selected pH value interval was from 1.32 to 6.32, as it is not advisable to work over pH 6.5 to avoid the formation of metal hydroxides. This figure illustrates that retention increases with the rise of pH to reach a plateau around 98% for pH superior to 4. The increase in pH leads to an increase in deprotoned carboxylic groups concentration, which favours the formation of macromolecular polymer–metal complexes, and subsequently an increase in metal rejection coefficients [28,29]. It can be also observed that permeate flux increases as far as pH increases. In fact, this behaviour can be explained in 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 [30]. At low pH, carboxylic functional groups (COOH) of polymer would not be dissociated and the poly(acrylic acid) (PAA) chain forms highly compact clusters, which are joined by short extended parts of a polymer chain whose microenvironment
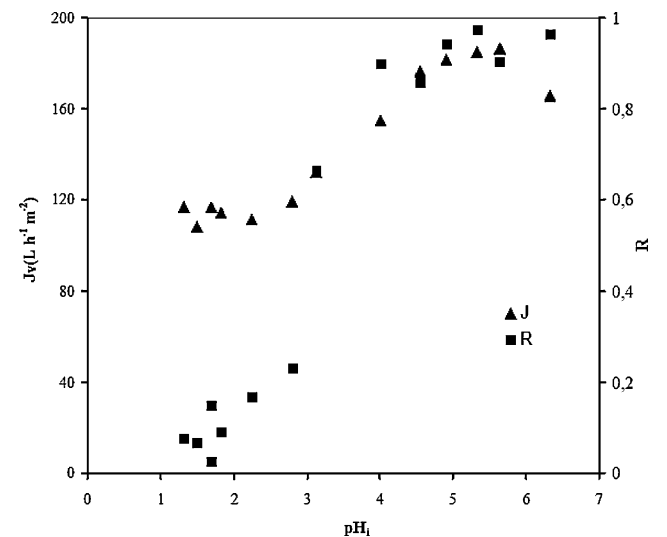

Fig. 6. Cadmium retention and permeate flux according to the pH at initial concentration of cadmium equal to 10^{-3} mol L^{-1} at $\theta = 30\,^{\circ}$C and $\Delta P = 2$ bar.

polarity is identical with that of hydrophobic areas of PAA. On the other hand, the membrane charge varies with the pH around its isoelectric point. At pH beyond isoelectric point the membrane is negatively charged. Associated with pH solution, carboxylic groups of polymer start dissociating and the presence of carboxylate anions (COO^-) is more important. The electrical charges existing in the molecules lead to apparition of intramolecular and intermolecular repulsion forces'.

This fact means expansion of polyelectrolyte chains, acquisition of a rod-like structure, and the lack of aggregation between polymer molecules.

4. Conclusion

In this paper, enhanced ultrafiltration by the addition of poly(ammonium acrylate), with two average molecular weights (8000 and 15 000 Da), for the removal of Cd(II) from aqueous solutions has been studied.

The resistance-in-series model was followed and membrane resistance, adsorption and concentration polarization during ultrafiltration was quantified. An effort has been made to evaluate these resistances independently at different operating conditions.

The variation of permeate flux as a function of the trans-membrane pressure for different feed concentrations of $PAmA_{15}$ were studied. It showed that the permeate flux increases with transmembrane pressure and decreases with the increase of polyelectrolyte concentration, insignificant polarization concentration phenomenon and negligible osmotic pressure were observed.

The study of ionic strength effect demonstrates that it decreases the retention of cadmium ions and increases the permeate flux. More than 99% of cadmium was retained for a $NaNO_3$ feed concentration less than 5×10^{-2} mol L^{-1}.

The pH effect study on the cadmium recovery revealed a maximum retention around 98% for pH 4. It can be also observed that permeate flux increases with increasing pH. These results can be explained by a conformational change on the polymer chains, a competitive adsorption between Na^+ or H^+ and Cd^{2+} on negatively charged polymer and the attenuation of the electrostatic repulsion.

References

[1] Awwa Membrane Technology Research Committee, Recent advances and research needs in membrane fouling, J. Am. Water Works Assoc. 97 (2005) 79.
[2] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.
[3] U. Danis, C. Aydiner, Investigation of process performance and fouling mechanisms in micellar-enhanced ultrafiltration of nickel-contaminated water, J. Hazard. Mater. 162 (2009) 577–587.
[4] B.R. Fillipi, L.W. Brant, J.F. Scamehorn, et al., Use of micellar-enhanced ultrafiltration at low surfactant concentrations and with anionic–nonionic surfactant mixtures, J. Colloid Interf. Sci. 213 (1999) 68–80.
[5] R.S. Juang, Y.Y. Xu, C.L. Chen, Separation and removal of metal ions from dilute solutions using micellar-enhanced ultrafiltration, J. Membr. Sci. 218 (2003) 257–267.
[6] C.W. Li, C.K. Liu, W.S. Yen, Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu(II) ions, Chemosphere 63 (2006) 353–358.
[7] H. Byhlin, A.S. Jonsson, Influence of adsorption and concentration polarisation on membrane performance during ultrafiltration of a non-ionic surfactant, Design 151 (2003) 21–31.
[8] L. Gzara, M. Dhahbi, Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants, Design 137 (2001) 241.
[9] X. Zhu, K.H. Choo, A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane, Colloids Surf. A: Phys. Chem. Eng. Aspects 312 (2008) 231–237.
[10] L. Song, Flux decline in crossflow microfiltration and ultrafiltration mechanisms and modelling of membrane fouling, J. Membr. Sci. 139 (1998) 183–200.
[11] C.W. Li, C.H. Cheng, K.H. Choo, W.S. Yen, Polyelectrolyte enhanced ultrafiltration (PEUF) for the removal of Cd(II): effects of organic ligands and solution pH, Chemosphere 72 (2008) 630–635.
[12] J. Sabaté, M. Pujolà, J. Llorens, Simulation of a continuous metal separation process by polymer enhanced ultrafiltration, J. Membr. Sci. 268 (2006) 37–47.
[13] M.K. Aroua, F.M. Zuki, N.M. Sulaiman, Removal of chromium ions from aqueous solutions bypolymer-enhanced ultrafiltration, J. Hazard. Mater. 147 (2007) 752–758.
[14] A. Tabatabai, J.F. Scamehorn, S.D. Christian, Economic feasibility study of polyelectrolyte-enhanced ultrafiltration (PEUF) for water softening, J. Membr. Sci. 100 (1995) 193–207.
[15] J. Llanos, A. Pérez, P. Canizares, Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration, J. Membr. Sci. 323 (2008) 28–36.
[16] P. Canizares, A. Pérez, R. Camarillo, R. Mazarro, Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process, J. Membr. Sci. 320 (2008) 520–527.
[17] P. Canizares, A. Pérez, R. Camarillo, J.J. Linares, A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents, J. Membr. Sci. 240 (2004) 197–209.
[18] X. Tan, W.K. Teo, K. Li, Removal of chromate ions from water using the polyelectrolyte-enhanced ultrafiltration process, Sep. Sci. Technol. 43 (2008) 477–489.
[19] S. Islamoglu, L. Yilmaz, Effect of ionic strength on the complexation of polyethyleneimine (PEI) with Cd^{2+} and Ni^{2+} in polymer enhanced ultrafiltration (PEUF), Design 200 (2006) 288–289.
[20] G. Champetier, Chimie macromoléculaire, Herman I (1972) 150–200.
[21] 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.
[22] 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.
[23] W.R. Bowen, P.M. Williams, Quantitative predictive modelling of ultrafiltration processes: colloidal science approaches, J. Colloid. Interf. Sci. 134 (2007) 3–14.
[24] X. Zhu, K.-Hg. Choo, A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane, Colloids Surf. A: Phys. Eng. Aspects 312 (2008) 231.
[25] S. Trizcinski, K.M. Varum, D.U. Staszewska, O. Smidsrod, M. Bohdanecky, Polymer 48 (2002) 171.
[26] M. Rumeau, F. Persin, S. Verdier, M. Persin, J. Sarrazin, Separation by coupling ultrafiltration and complexation of metallic species with industrial water-soluble polymers. Application for removal or concentration of metallic cations, J. Membr. Sci. 73 (1992) 313.
[27] P. Canizares, A. Pèrez, R. Camarillo, J.J. Linares, A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents, J. Membr. Sci. 240 (2004) 197–209.
[28] 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.
[29] T.B. Choe, P. Masse, A. Verdier, M.J. Clifton, Membrane fouling in the ultrafiltration of polyelectrolyte solutions: polyacrylic acid and bovine serum albumin, J. Membr. Sci. 26 (1986) 17.
[30] B. Bednar, J. Truena, P. Svoboda, S. Vajda, V.K. Fidler, K. Prochazka, Macromolecules 24 (1991) 2054.