Cadmium and zinc removal from water by polyelectrolyte enhanced ultrafiltration

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Abstract. The efficiency of two metal ions (cadmium, zinc) removal from aqueous solutions by ultrafiltration (UF) and Polymer Enhanced Ultrafiltration (PEUF) processes were investigated in this work. The UF and PEUF studies were carried out using an ultrafiltration tangential cell system equipped with 5.000 MWCO regenerated cellulose. A water-soluble polymer: the polyacrylic acid (PAA) was used as complexant for PEUF experiments. The effects of transmembrane pressure, pH, metal ions and loading ratio on permeate fluxes and metal ions removals were evaluated. In UF process, permeate fluxes increase linearly with increasing pH for different transmembrane pressure, which may be the consequence of the formation of soluble metal hydroxyl complexes in the aqueous phase. In PEUF process, above pH 5.0, the Cd(II) retention reaches a plateau at 90% and Zn(II) at 80% for $L = 5$. Also, cadmium retention at different L is greater than zinc retention at pH varying from 5.0 to 9.0. In a mixture solution, cadmium retention is higher than zinc for different loading ratio, this is due to interactions between carboxylic groups of PAA and metal ions and more important with cadmium ions.

Keywords: cadmium; zinc; polymer enhanced ultrafiltration; removal efficiency; ultrafiltration

1. Introduction

Heavy metal contamination water has become an important problem in recently years. Most hazardous heavy metals exist in environmental water under trace or ultra-trace amounts, which requires establishing highly sensitive analytical methods.

Among many separation techniques, membrane separation is an efficient and widely applied separation process. In the last 20 years, membrane filtration such as; ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been shown to be promising for removal or recuperation of metals from aqueous solutions (Juang and Chiou 2000, Aliane *et al.* 2001, Yurlova *et al.* 2002, Pastor *et al.* 2002, Zhang and Xu 2003, Petrov and Nenov 2004, Baraket and Schmidt 2010, Baharuddin *et al.* 2014). Reverse osmosis or at least nanofiltration can be used due to the

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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. It is of particular interest that the use of ultrafiltration is an alternative treatment for the ionic metals removal.

approaches when explaining different affinities of these polymers with metal ions, to the de One of the developed water treatment processes is Polyelectrolyte Enhanced UltraFiltration (PEUF) that has been shown to be an efficient technology for the removal of heavy metals even at low concentrations. The polyelectrolyte enhanced ultrafiltration technique uses solutions of polymers combined with membrane filtration. Its principle fixation of metallic ions on macromolecular species, which is performed to increase their molecular weight. As shown in Fig. 1, complexes of metal ions with polymer are retained by the membrane, which unable to pass through the ultrafiltration membrane, while free ions are eluted through the membrane. These compounds, which then become larger ore sizes than elected membrane, can be retained then water will be purified, Trivunac and Stevanovic (2006a, b).

When metal ions mixtures solutions are put in contact with polymer solution, a profile of the retention of different metal ions by polymer during filtration can be obtained Villoslada and Rivas (2003).

The characteristic of the polymer groups has significant effect on solution mixture property and eventually affects the ultrafiltration (UF) performance. Polyelectrolytes having several active anionic groups from complexes with mono or multivalent metal ions, Mondal *et al*. (2011).

A great quantity of papers prefer an analytical triment of searching for a technological development of this binding phenomenon (Rivas and Villoslada 1998, Villoslada and Rivas 2002, 2003, Rivas *et al*. 2004, Ennigrou *et al*. 2009). Arshad *et al*. (2014), Palencia *et al*. (2009) reported that the polymer-metal complexes-membrane interaction plays a major role simultaneously with the membrane-metal ions interactions on the ultrafiltration of metal ions solution.

The objective of this study was to investigate the removal of cadmium and zinc from aqueous solution by complexation-ultrafiltration with PAA. Experiments were performed as a function of transmembrane pressure, pH, metal ions and loading ratio on permeate fluxes and metal ions removals.
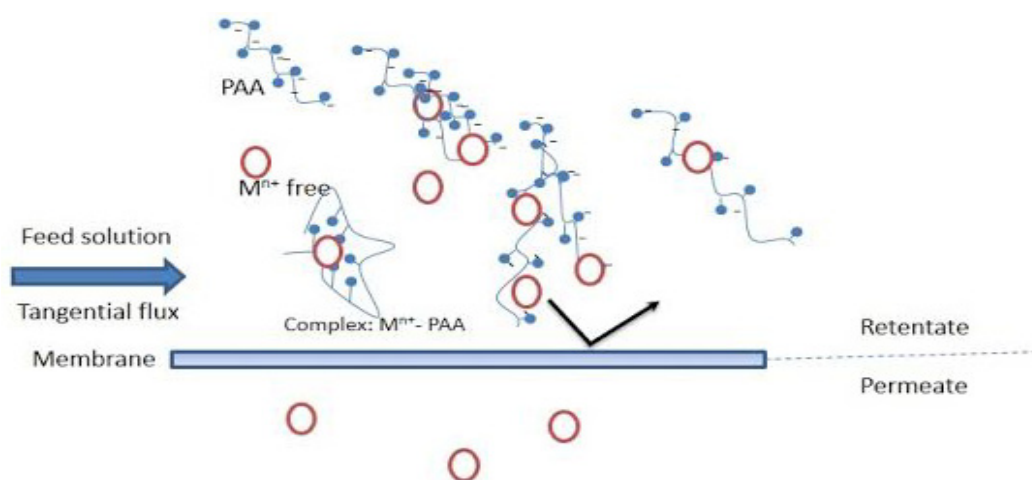

Fig. 1 Scheme of the process of metal-ion retention by PEUF systems

2. Materials and methods

2.1 Experimental set up and procedure

Cross-flow membrane filtration was carried out with a tangential cell system (Labscale TFF). Organic regenerated cellulose membrane (CR) was used for all the PEUF experiments. Molecular weight cut-off (MWCO) of this membrane was 5 kDa (PTGC OMS 5). Its effective filtration area was 50 cm^2. Both membrane and ultrafiltration system were supplied by Millipore incorporation (Germany). 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. Ultrafiltration experiments were conducted at room temperature (~25°C).

Samples to be analyzed were taken at the inlet (feed solution) and at the outlet of the system (permeate).

A scheme of the experimental ultrafiltration system is shown in Fig. 2.

2.2 Reagents

All reagents were analytical grade; they were purchased from Sigma Aldrich.

Poly(acrylic acid) (PAA) with molecular weight 10^5 Da, was used as the complexation agent. The filtration of an aqueous solution of PAA with a 5 kDa membrane indicates that the polymer was retained by the membrane and doesn't gets into the permeate.

Cadmium chloride (CdCl$_2$. H$_2$O) and zinc chloride (ZnCl$_2$) salts were used to prepare solutions with known amount of compounds. Milli-Q water was used throughout.

The pH value was adjusted using NaOH or HCl as needed. The background electrolyte of the solution was adjusted (0.05 mol L^{-1}) by adding appropriate NaCl.
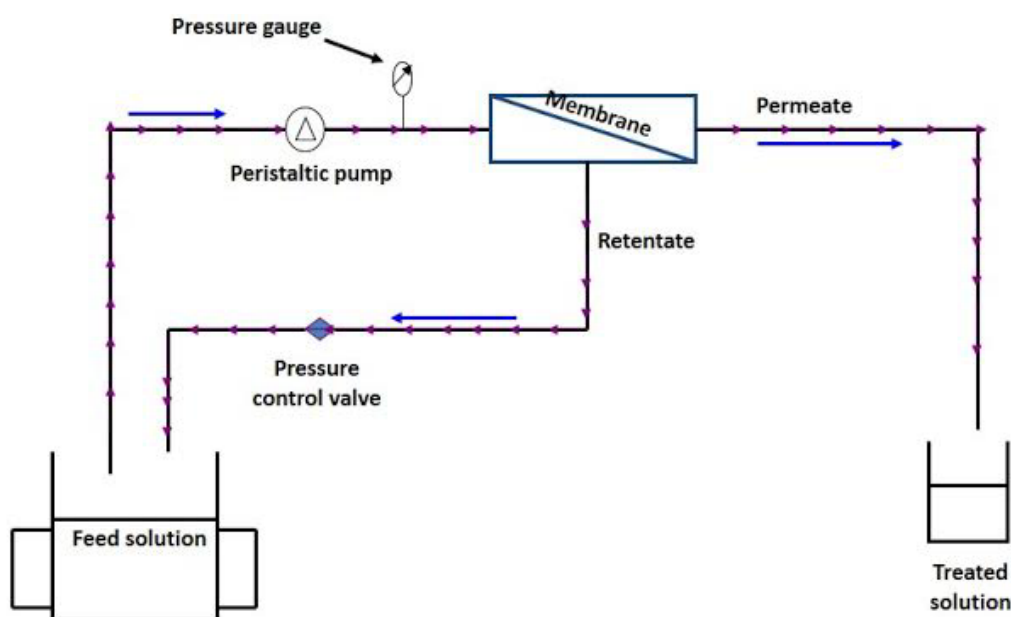

Fig. 2 Experimental ultrafiltration

2.3 Analytical methods

Samples were analysed to determine cadmium and zinc concentrations using the "Analytical Jena AAS vario 6"atomic absorption spectrophotometer. Measurements were taken for each sample, by direct aspiration into air acetylene flame. The instrument was instructed to give the mean value and standard deviations of three readings as the final reading of each sample.

654 pH-meter (Metrohm AG, Switzerland) was used for measuring pH solutions.

2.4 Data analysis

Permeate flux was calculated using Eq. (1)

$$J_v \left(Lh^{-1}m^{-2}\right) = \frac{v_p}{S.t} \tag{1}$$

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

The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's Law following Eq. (2)

$$J_w \left(Lh^{-1}m^{-2}\right) = L_p.\Delta P \tag{2}$$

L_p is the permeability of solvent, P is the transmembrane pressure.

Retention (R) was calculated as below to show the retention of metal ions, we have used the observed retention as defined in Eq. (3)

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right).100 \tag{3}$$

Where C_p and C_f are the concentrations (mol L^{-1}) of metal ions in the permeate and feed solution, respectively.

Loading ratio (L) is calculated as following to indicate the concentration ratio of poly (acrylic acid) (C_{PAA}) as well as metal ions concentration (C_M^{2+}).The observed loading ration was defined as Eq. (4)

$$L = \left(\frac{c_{pPAA}}{c_{M2+}}\right) \tag{4}$$

3. Results and discussions

3.1 Pure water membrane permeability

The pure water permeability (L_p) of the membrane was measured to characterize the membrane.

In the theory and taking into account the Eq. (2), pure solvent (water) flux should be proportional to transmembrane pressure and a plot of (J_W) versus applied pressure (P) should give a linear shape characterized by a slope known as (L_p). It is obtained by measuring the permeate
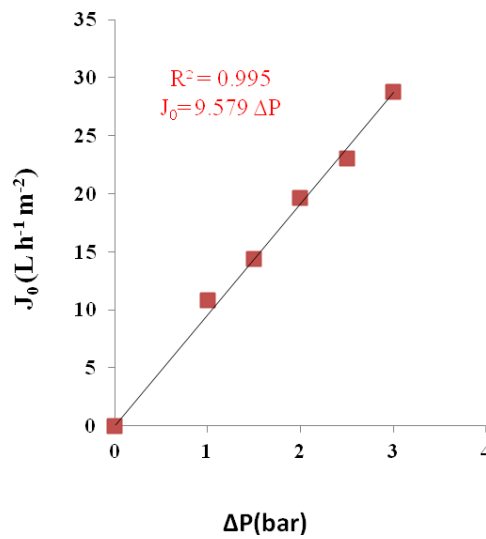
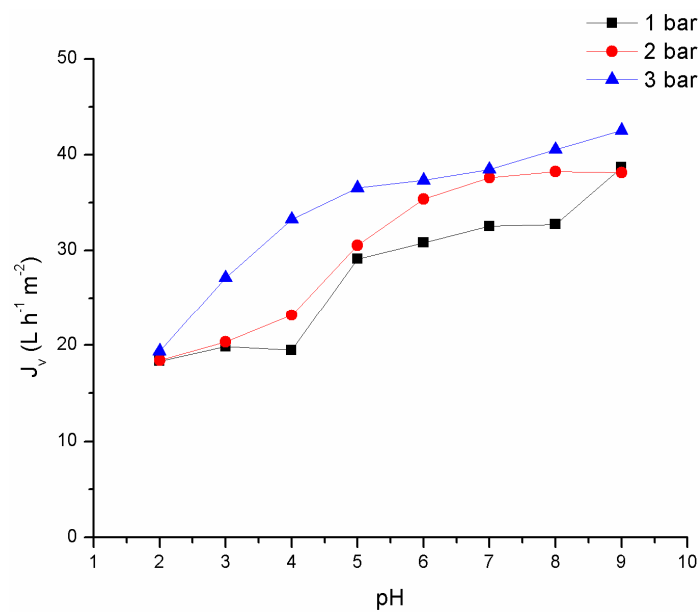Fig. 3 Permeate flux of water as a function of transmembrane pressure

Fig. 4 Permeate flux as a function of pH for different transmembrane pressure, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}

flow rate versus time and transmembrane pressure. The permeability of membrane studied was measured under different transmembrane pressure.

As shown in Fig. 3, membrane permeability (L_p) was found to be 9.579 (L $h^{-1}m^{-2}$ bar^{-1}) which was in the range of ultrafiltration membranes. This value will be considered as a reference in the remainder of this study. The systematic verification of this value can account for the effect of
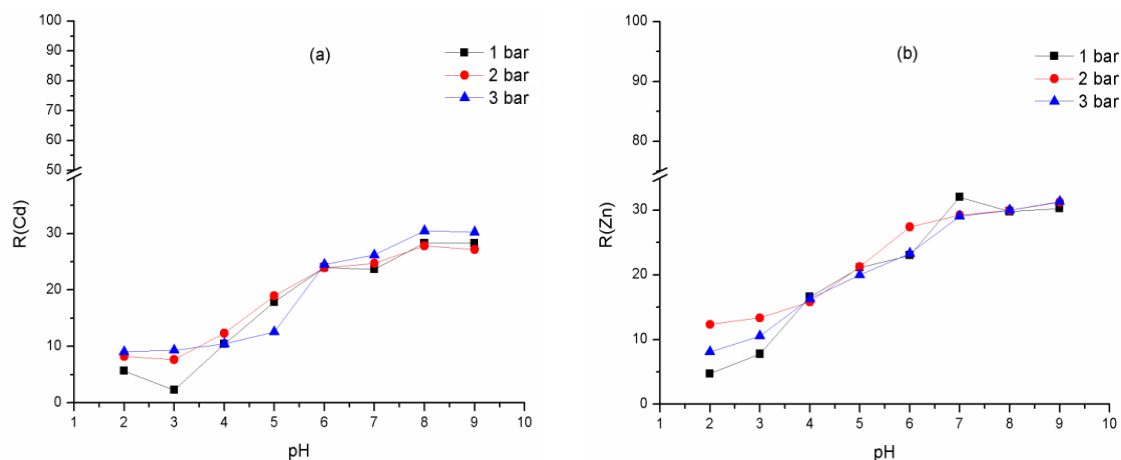
Fig. 5 (a) Cadmium; and (b) Zinc retention as a function of pH for different transmembrane pressure

concentration polarization that may occur during experimentation.

3.2 Ultrafiltration experiments

3.2.1 Effect of transmembrane pressure

The variation of permeate flux versus pH for different transmembrane pressure, was investigated at 10^{-3} mol L^{-1} cadmium and zinc ions concentrations. The variation of permeate fluxes is given in Fig. 4.

Initially, the permeate fluxes increase linearly with increasing transmembrane pressure, we can observe an increase in the permeate flux with increasing pH (beyond pH 5, flux is 20% higher than flux at pH 2). Indeed, at low pH, free metal ions (Cd(II) and Zn(II)), pass through the membrane, permeate fluxes increase for pH beyond 5, which may be the consequence of formation of soluble metal hydroxyl complexes in the aqueous phase (Alpatova *et al*. 2004, Arthanareewaran *et al*. 2007).

On the other hand, the variations of cadmium and zinc retention according to pH at different transmembrane pressure are given respectively in Fig. 5(a) and (b).

These figures show that cadmium and zinc retention increases with the increase of pH and transmembrane pressure, retention increases drastically beyond pH 5, but remains low. A maximum retention was observed at 3 bar transmembrane pressure, which values are nearly 30% for both metals.

At high pH values, the high retention can be explained by the formation of hydroxides metals complexes. In the other hand, at lower pH, the observed retention may be due to the electrostatic repulsion and steric exclusion effect described by the Ferry law (Ferry 1936). Also, the retention of metal ions at different transmembrane pressure can presumably be partly attributed to the presence of some small-size pores in the membrane (Aliane *et al*. 2001).

According to these results, experimental condition for transmembrane pressure will be fixed at 3 bar for remaining experiments.

3.2.2 Effect of pH of UF process

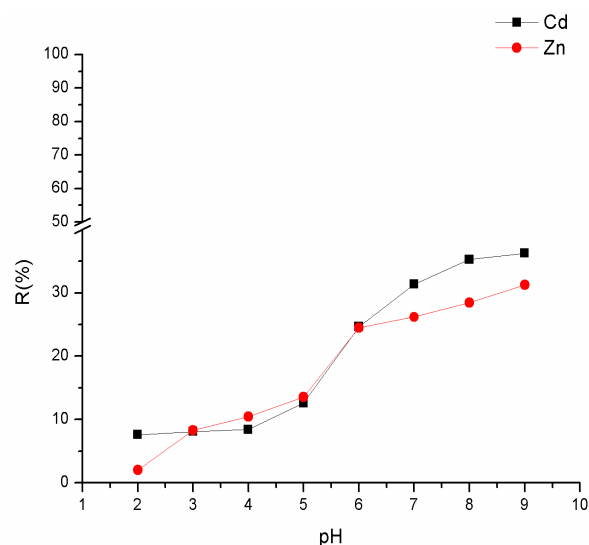The retention of cadmium and zinc was studied at different pH values ranging from 2 to 9 and

Fig. 6 Metal ion retention as a function of pH, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}, $P = 3$ bar
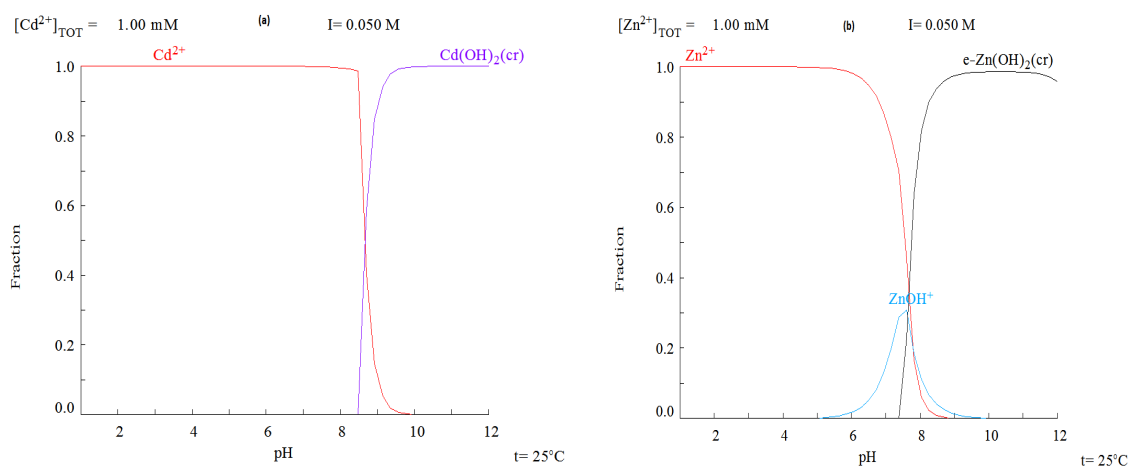

Fig. 7 Chemical speciation diagram of a 10^{-3} mol L^{-1}: (a) Cadmium; and (b) Zinc solutions

10^{-3} mol L^{-1} metal ions solution and 0.05 mol L^{-1} ionic strength.

Effect of feed solution pH on retention of Cd(II) and Zn(II) is illustrated in Fig. 6.

For solution containing only one metal, retention of cadmium is slightly higher than zinc. The two metals have the same behaviour. Their retentions increase with the increase of pH.

Speciation diagrams are very important for the interpretation and the understanding reactivity of metal ions in solution. They help to identify forms in which ions are present in solution as a function of pH. Throughout investigation, Medusa Software Version 2.25, was used to generate species diagrams for Cd(II) and Zn(II) 10^{-3} mol L^{-1} ions concentration and 0.05 mol L^{-1} ionic strength at variable pH (Medusa Software).

The speciation diagrams for Cd(II) and Zn(II) are given respectively in Figs. 7(a) and (b).
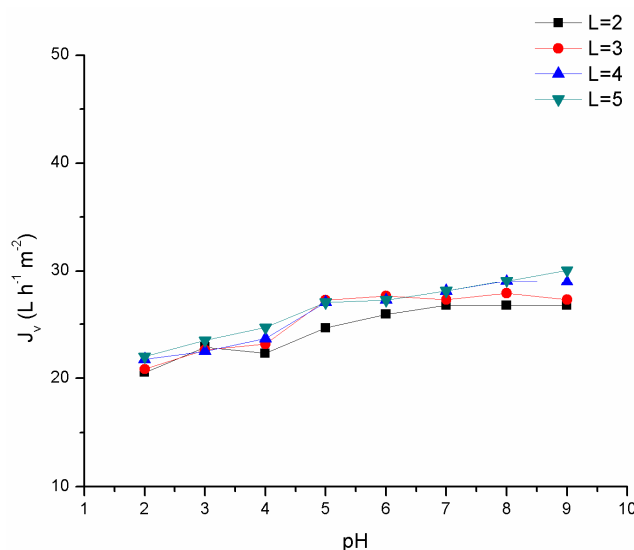
Fig. 8 Permeate flux as a function of pH for different loading ratios (L) $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}, $P = 3$ bar

As shown in this Fig. 7(a), cadmium exists in solution under two species namely Cd^{2+} and $Cd(OH)_2$ and the proportions of these species vary with pH. Up to pH of 2.0, the major species is Cd^{2+}, which represents 100% of the total cadmium. In this range of pH cadmium ions can be transported through membranes. This species disappears at pH 8.5 letting place to the formation of cadmium hydroxides. This form can be retained by membranes and cadmium retention increases consequently.

In Fig. 7(b) the speciation diagram of Zn(II) shows that soluble Zn charged hydroxides exist when pH < 6.7. In this range of pH Zn ions can be transported through membranes. As consequence, Zn removal rates are minimal. The Zn speciation diagram shows also that only non-charged Zn hydroxide form can exist for pH = 6.7 and more. This compound cannot be transported by ultrafiltration process. For that reason Zn removal was very high. Also, at high pH some scaling problems can appear. An accumulation of Zn hydroxides, in the neighbourhood of the membrane, caused by concentration polarisation and deposit layer formation, can be expected. An interaction (adsorption) with the membrane material can occur thus a stable layer of these species on membrane will be formed. These phenomena have a great effect on the ultrafiltration performance. They reduce efficiency of process and increase the power of consumption.

3.3 Polyelectrolyte enhanced ultrafiltration experiments

3.3.1 Effect of loading ratio on retention and permeate flux

The formation of metallic complexes with a polymer is depending on pH and polymer concentration, polymers affects the formation of cations-polymer complex and decide the maximum effectiveness in PEUF process.

In order to determine the effects of loading ratio (PAA/M^{2+} (polyacrylic acid/Cd or polyacrylic acid/Zn)) on metals removal efficiency, the experiments were performed with 10^{-3} mol L^{-1} Cd and
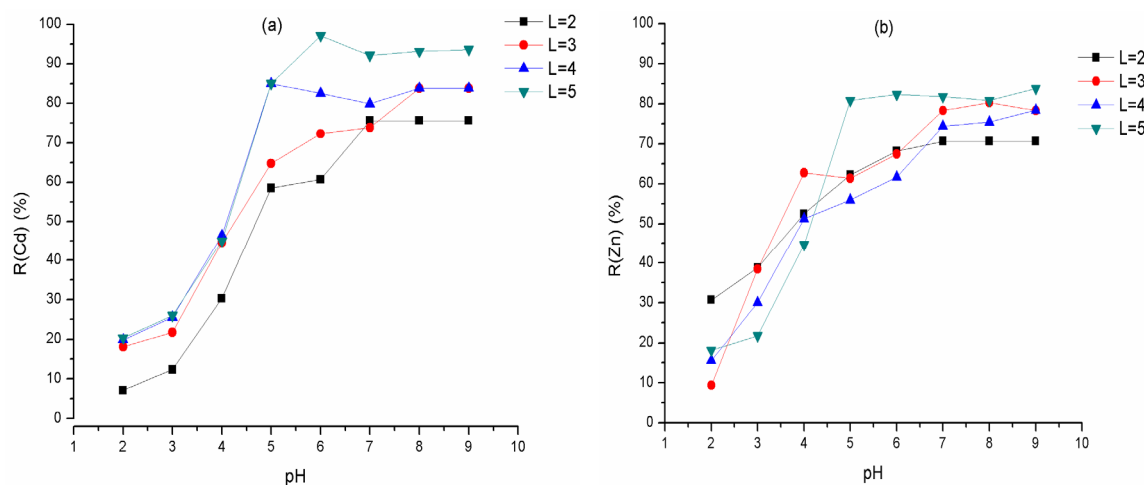
Fig. 9 (a) Cadmium; and (b) Zinc retention as a function of pH for different loading ratio, $[Cd^{2+}]$ = 10^{-3} mol L^{-1}, $[Zn^{2+}]$ = 10^{-3} mol L^{-1}, P = 3 bar

Zn concentrations and 3 bar transmembrane pressure.

As indicates Fig. 8, the permeate fluxes at different PAA/M^{2+} as a function of pH were ploted. The effect of loading ratio (L) on Cd and Zn permeate fluxes is presented at various pH from 2 to 9.

As shown in this figure, pH has a small effect on permeate flux with values fluctuating around 20-30 L h^{-1} m^{-2}; the permeate fluxes in the PEUF process are all lesser than in UF process, indicating that relatively large pores in the UF membrane probably reject or absorb very small amount of cadmium or zinc (Shao *et al*. 2013).

This behaviour can be explained by the fact that ultrafiltration membranes are permeable to water and salt. And then, due to the unequal ion distribution, osmotic and swelling pressures between the two phases exist, Bowen and Williams (2007).

The effect of loading ratio on permeate fluxes can be explained by the conformational changes undergone by polymer molecule structure, interactions between polymer and molecules as well as interactions between polymer and membrane, Ennigrou *et al*. (2014).

On the other hand, the effect of loading ratio on cadmium and zinc retention was investigated in the same conditions. Figs. 9(a) and (b) show the pH effect on the retention of cadmium and zinc at different PAA/M^{2+}.

At low pH, the competition between H^+ and divalent metal ions to bond with ligand is established. As noticed, the retention of metal ions increases with increasing the pH. At low pH, where the majority of the acid groups are protonated, affinity towards metal ions is poor and the stability of the complex is low. As the pH increases, the affinity and stability of polymer–metal complexes increase.

With an increase of pH, complexation process is more effective, beyond pH 5.0 retention coefficient of cadmium and zinc complexes is about 80%. Indeed, at pH above 5, retention coefficient is significantly high in the presence of complexing agent due to complexation effect, but varies with changing loading ration (*L*). It is also observed, that at low *L* (such as 2), cadmium retention is low when pH varies from 2 to 5; at high *L*, cadmium and zinc retention are also low if
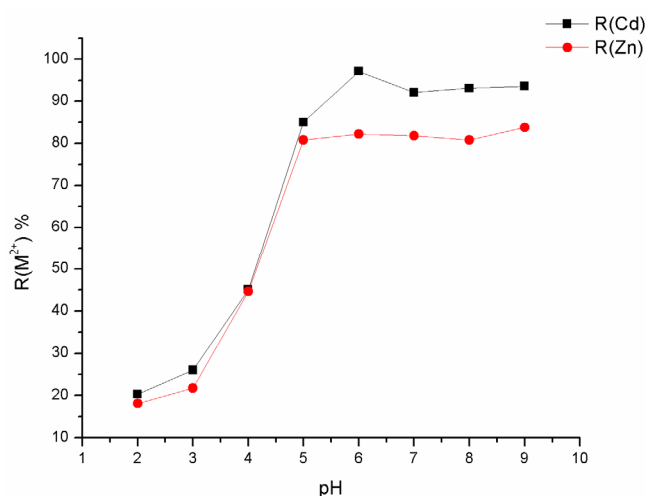
Fig. 10 Cadmium and Zinc retention as a function of pH $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}, $P = 3$ bar, $L = 5$

pH is reduced to less than 5.

Above pH 5, the Cd(II) retention reaches a plateau at 90% and Zn(II) at 80% for $L = 5$. An 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 retention, Villoslada *et al*. (2001). At the same time, cadmium retention at different loading ratio is greater than zinc retention when pH varies from 5.0 to 9.0.

3.2.2 Effect of pH on PEUF process

As shown previously, pH is one of the most important parameters determining the binding capacity of Cd and Zn with PAA. The metal ions retention experiments at loading ratio $L = 5$ and a 3 bar transmembrane pressure were investigated at different pH values.

Considering Figs. 9(a) and (b), optimum PAA/M^{2+} ratio was chosen to be 5 and economical cost of PAA for further complexation-ultrafiltration process for cadmium and zinc retention using PAA as the complexation agent.

Fig. 10 shows variation of cadmium and zinc retention as a function of pH. It shows that retention increases with the rise of pH to reach a plateau around 97% for cadmium and 83% for zinc at pH 5. We observed that cadmium retention is higher than zinc; this can attributed to be the stability of the formed M^{2+}-PAA complex which is pH dependent. The rejection of metals depends strongly on pH because to higher binding with the polymeric ligands at higher pH values. At low pH, the affinity of PAA towards the metal ions is weak, due to the presence of positive charges and so stability of complex is low, Baraket and Schmidt (2010).

3.3.2 Ultrafiltration of mixture metal ions solution

In previous research studies, Ennigrou *et al*. (2009), Jellouli *et al*. (2010), we studied recovery and selective separation of metal ions using polyacrylic acid (PAA) as chelating agents. Although the study did not achieve a selective separation, it revealed a working method valid for every system involving a pair of metal ions complexed by a polymer (Jellouli *et al*. 2010).
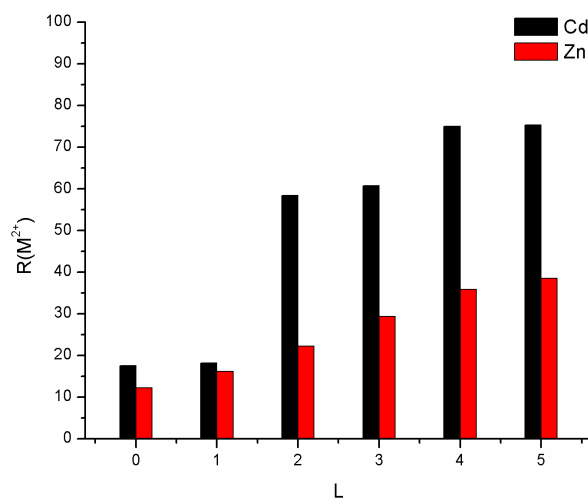
Fig. 11 Retention of cadmium and zinc ions in mixture solution according to loading ratio,
$[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}, $\Delta P = 3$ bar, pH = 5

In the presence of both metal ions in solution, a competitive complexation of metal ions occurs. Fig. 11 shows the retention of cadmium and zinc ions in a mixture solution according different loading ratio at pH 5 and 3 bar transmembrane pressure. It shows that cadmium retention is higher than zinc for different L. In the absence of PAA ($L = 0$) cadmium retention is always greater than zinc, this result was previously shown in the case of single metal ion solution (see Section 3.3.1). On the other hand, the interactions between carboxylic groups of PAA and metal ions are observed and more important with cadmium in solution.

Similar behaviour was observed with cadmium and zinc ions concerning the effects of pH and the presence of polymer. As can be seen the rejection coefficient is higher in the presence of complexing agent than in the absence of ligand (Trivunac and Stevanovic 2006a, b).

At the same time, contrarily to Zn ions, the retention coefficient of Cd ions increases with the increase of L, reaching 90% at 10^{-4} mol L^{-1} PAA concentration. This indicates that Cd-PAA complex is less stable than zinc one. It may be explained by the fact that the d electrons of cadmium are more tightly held and less available for π bonding, requesting the high excess of complexing agent to form a complex.

4. Conclusions

In this paper, UF and PEUF processes were investigated on cadmium and zinc retention from aqueous synthetic solutions. The results from the present study showed that the removal of metal ions by UF and PEUF depends on several parameters such as a transmembrane pressure, pH, and loading ratio.

In UF process (in absence of PAA), permeate fluxes increase linearly with increasing transmembrane pressure for different pH, permeate fluxes increase beyond pH 5.

Cadmium and zinc retention increases with the increase of pH and transmembrane pressure, retention increases drastically beyond pH 5, but remains low.

In PEUF process (in presence of PAA), above pH 5.0, Cd(II) retention reaches a plateau at 90% and Zn(II) at 80% for $L = 5$. Also, cadmium retention at different L is greater than zinc retention at pH varying from 5.0 to 9.0.

The best performed obtained by PEUF process was observed at transmembrane pressure $P = 3$ bar, loading ratio $L = 5$ and pH = 5.

In a mixture solution, cadmium retention is higher than zinc for different loading ratio, these interactions between carboxylic groups of PAA and metal ions are more important in the case of cadmium ions. Nevertheless, retention coefficient of Cd ions increases with the increase of L, reaching 75% at $L = 5$. This indicates that the Cd-PAA complex is less stable than zinc one.

The industrial effluents should be considered to study the effects of other metals and substances on the separation of target metal ions. Membrane fouling characterization, chemical regeneration of the polymer, polymer behaviour with pH changes should also be investigated.

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