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Removal of heavy metals from aqueous solution by polyacrylic acid enhanced ultrafiltration

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ABSTRACT

One of the recently developed water treatment processes is the polyelectrolyte-enhanced ultrafiltration (PEUF). This technique combines a membrane filtration process (ultratfiltration) and a cation–polyectrolyte complexation technique. PEUF is shown to be an efficient technology for the removal of heavy metals from liquid effluents even at low concentrations. In this proposal, the removal of three heavy metals (cadmium, copper and zinc) from aqueous solutions by PEUF process was investigated. The poly(acrylic acid) (PAA) with an average molecular weight 100 kDa was used as complexing agent. The ultrafiltration experiments were performed using a tangential cell system equipped with a polyethersulphone membrane having a 10.000 molecular weight cut-off (MWCO). To improve the retention of the heavy metal ions, the effect of some operating parameters and solution characteristics were studied. For different PAA concentrations, this study showed that all permeate fluxes increased linearly by increasing transmembrane pressure. For the three studied metals, the best retentions were observed at 2×10^{-3} mol L^{-1} PAA concentration, 3 bar transmembrane pressure and pH above 5. The removal of cadmium, copper and zinc exceeded, respectively, 80, 93 and 70%.

Keywords: Cadmium; Copper; Zinc; Polyacrylic acid; Removal of ions; Polyelectrolyte-enhanced ultrafiltration

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1. Introduction

Heavy metals that are going out to the environment caused by human activity are or will be in aqueous solution, which must be removed before water recycling or discharging directly into surface (or sometimes subsurface) water. Thus, people need effective water cleaning methods. 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 [1–6] and PEUF [7–10] combine ultrafiltration with the

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presence of water-soluble surfactants and polymers, respectively.

Membrane processes were employed 30 years ago in order to retain inorganic ions (reverse osmosis, electrodialysis, etc.), but they lacked selectivity. For this reason, new methods like liquid membranes, polymer and MEUF have been developed [11–13].

Among the various processes for heavy metal removal from water, the technique of complexation–membrane filtration proved to be a promising alternative to technologies based on precipitation and ion exchange. Numerous studies on this subject have been described in past decade [14–16].

In the present paper, a polyelectrolyte enhanced ultrafiltration (PEUF) is the combination of two phenomena: binding of metal ions to a water-soluble polymer, 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 [17–20].

The aim of this study is to evaluate the removal efficiency of cadmium, copper and zinc ions using poly(acrylic acid) (PAA), with average molecular weight (100 kDa) as polyelectrolyte chelating agent. The effect of transmembrane pressure, polyelectrolyte concentrations and pH on the process efficiency, related to the retention of Cd(II), Cu(II) and Zn(II), is investigated in this paper. Selectivity was studied using a solution containing three metal ions.

2. Methods

2.1. Ultrafiltration experiments

In all experiments, the feed volume was 250 mL and the first 25 mL of permeate were discarded. During the ultrafiltration process; temperature and feed flow rate (up to $0.5\,\mathrm{m\,s^{-1}}$) were kept constant and a transmembrane pressure was varied from 1 to 3 bar. The feed solution was kept stirred and circulated by means of the pump, then passed through the membrane cartridge. Polyethersulphone membrane with molecular weight cut-off (MWCO) of 10 kDa and an effective filtration area of $50\,\mathrm{cm}^2$ were used (PTGC OMS 10, Millipore).

The retention values were calculated from the formula:

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

where C_p is the concentration of metal ion in permeate and C_f is the concentration of metal ion in feed solution. The used membrane was immediately flushed with deionized water after ultrafiltration. The pure water flux was always measured before every ultrafiltration process in order to assess the cleanness of the membrane.

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

$$J_w = L_p^0 \Delta P \tag{2}$$

L_p^0 is the permeability of solvent and ΔP is the transmembrane pressure.

$$J_v = \frac{V_p}{S \cdot t} = L_p \Delta P \tag{3}$$

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

L_p is the permeability of aqueous solution.

2.2. Membrane permeability

A pure water flux (J_w) measurement as a function of transmembrane pressure (ΔP) for ultrafiltration membrane was carried out (Fig. 1). Using Eq. (2), the membrane permeability (L_p^0) was found to be 225.15 L $\mathrm{h^{-1}\,m^{-2}\,bar^{-1}}$ which was in the range of ultrafiltration membranes. The L_p^0 values were used as references to evaluate cleaning procedures, it was determined prior to each experiment.

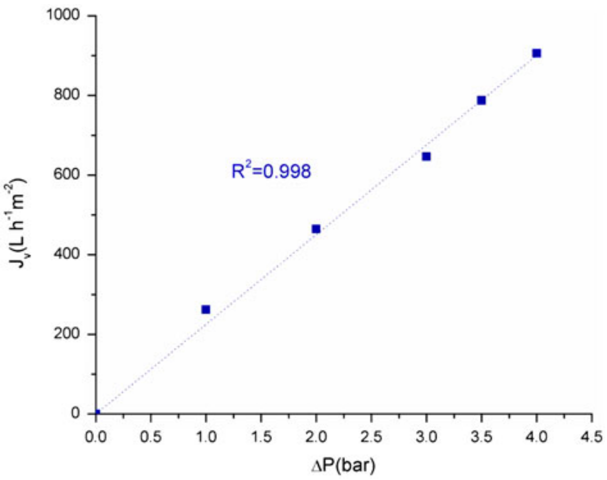

Fig. 1. Permeate flux of water as a function of transmembrane pressure.

2.3. Materials and analysis

The chemical reagents used in the experiments were PAA was used in this study. Its molecular weight is chosen equal to 100,000 Da, cadmium chloride ($CdCl_2{\cdot}2H_2O$), copper chloride ($CuCl_2{\cdot}2H_2O$) and zinc chloride ($ZnCl_2{\cdot}2H_2O$). In the study of the effect of pH, sodium hydroxide and chloride acid were used. All chemicals used are of analytical grade supplied by sigma Aldrich. Deionized water obtained from deionization system Milli-Q gradient unit (Millipore), it was used for dilution and preparation of feed solution. The concentrations of different metal ions were measured by means of atomic absorption spectrophotometry (AAS) using the Analytical Jena AAS vario 6 atomic absorption spectrophotometer.

3. Results and discussions

3.1. Ultrafiltration of metal ions solution

Fig. 2(a) represents the variation of cadmium, copper and zinc retention as a function of the transmembrane pressure for a feed metal ions concentration equal to 10^{-3} mol L^{-1} at 25˚C. It shows that the metal retention remained nearly constant at the values of 4, 6 and 10%, respectively. In order to enhance these rejections, it was interesting to add a polyelectrolyte as complexing agent. PAA has been used to retain metals by the PEUF process.

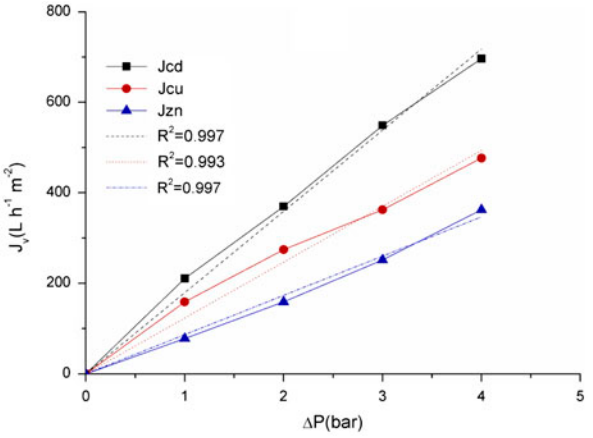

Fig. 2b. Permeate flux according to the transmembrane pressure, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Cu^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}.

The variation of permeate fluxes as a function of transmembrane pressure is given in Fig. 2(b). All permeate fluxes are proportional to transmembrane pressure, as it could be predicted by Eq. (3). The slopes of the straight lines are aqueous cadmium, copper and zinc solutions permeability, respectively ($L_p = 179.47$ L h^{-1} m^{-2} bar^{-1}, $L_p = 123.39$ L h^{-1} m^{-2} bar^{-1} and $L_p = 86.67$ L h^{-1} m^{-2} bar^{-1}). It implies that the presence of a metal ions solution does not generate significant additive resistance, generally manifested when solutes were filtered by the membrane.

3.2. Effect of PAA concentration

The effect of poly(acrylic acid) concentration was investigated at a fixed heavy metal ions concentration of 10^{-3} mol L^{-1}, PAA concentrations varies from 10^{-3} to

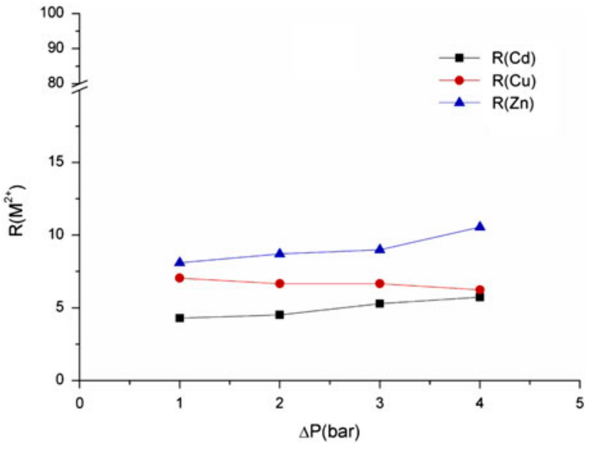

Fig. 2a. Retention of metal ions according to the transmembrane pressure, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}, $[Cu^{2+}] = 10^{-3}$ mol L^{-1}, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}.

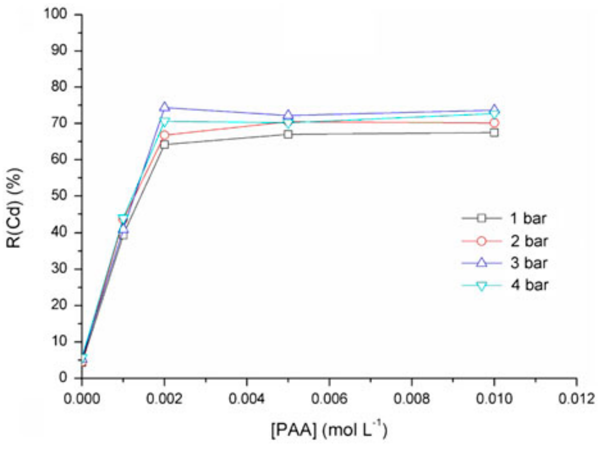

Fig. 3a. Cadmium retention as a function of PAA concentrations at different transmembrane pressure, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}.

10^{-2} mol L^{-1} and the transmembrane pressure was varied from 1 to 4 bar.

The variations of cadmium, copper and zinc retention vs. PAA concentrations are given, respectively in Figs. 3(a)–3(c). It shows that heavy metals retention increases with the increase of transmembrane pressure and PAA concentrations until to 2×10^{-3} mol L^{-1}.

Beyond this concentration, retentions of all heavy metals remained practically constant. This is mainly attributed to concentration polarisation, membrane fouling, osmotic pressure, precipitation and formation of a gel layer on the membrane surface [21].

The maximum rejection was obtained at $\Delta P = 4$ bar for all studied heavy metals. The rejections of Cd, Cu and Zn were 73, 80 and 70%, respectively for 2×10^{-3} mol L^{-1} PAA concentration.

3.3. *Effect of transmembrane pressure*

In Figs. 4(a)–4(c) the variations of permeate flux as a function of the transmembrane pressure for different feed concentrations of PAA are displayed. They show that the permeate flux increases with transmembrane pressure and decreases when PAA concentration increases from 10^{-3} to 10^{-2} mol L^{-1}. This behaviour can be explained by increasing the thickness of the layer polarization, the formation of binding bridges between the groups of PAA and the membrane is possible and could causes a fouling by: the metal ions- PAA aggregation in solution and by stronger PAA–surface interactions in the presence of divalent metal ions [22]. Consequently, an additional resistance to flow through membrane is observed and some membrane properties are modified (e.g. permeability, hydrophobic/hydrophilic relation, roughness and pore size distribution).

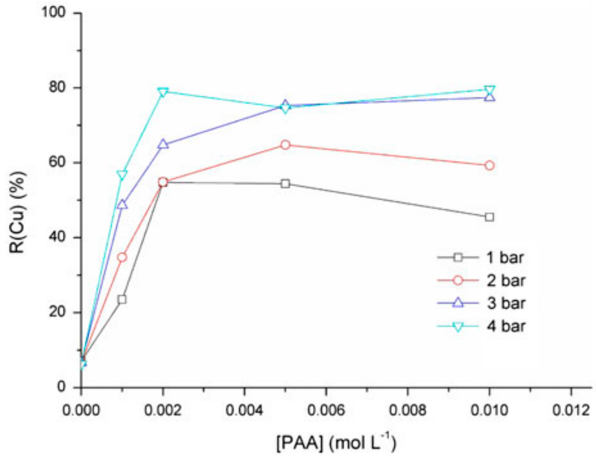

Fig. 3b. Copper retention as a function of PAA concentrations at different transmembrane pressure, $[Cu^{2+}] = 10^{-3}$ mol L^{-1}.

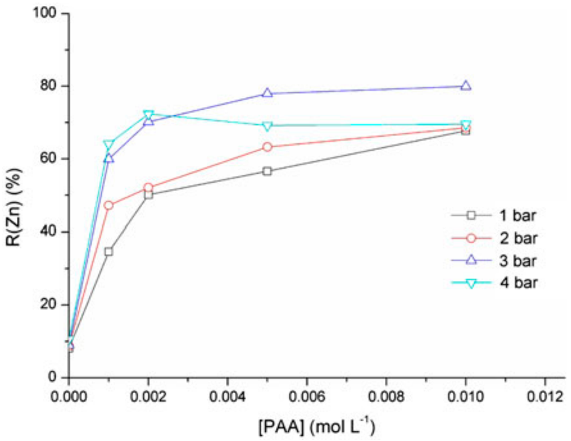

Fig. 3c. Zinc retention as a function of PAA concentrations at different transmembrane pressure, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}.

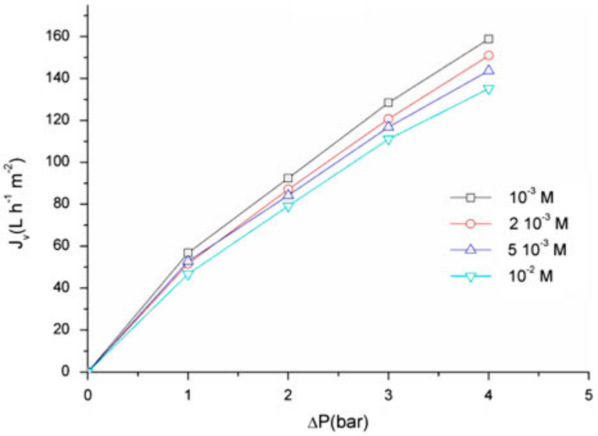

Fig. 4a. Permeate flux as a function of transmembrane pressure at different PAA concentrations, $[Cd^{2+}] = 10^{-3}$ mol L^{-1}.

On the other hand, the variation of heavy metal retention as a function of transmembrane pressure at a fixed heavy metal ions concentration of 10^{-3} mol L^{-1} and PAA concentration of 2×10^{-3} mol L^{-1} is depicted in Fig. 5. This figure shows that the retention of metallic ions increases with an increase of transmembrane pressure. Retention rises and reaches 75, 80 and 77% for cadmium, copper and zinc, respectively. A best retention is observed at 3 bar. Beyond this value, the rejection coefficient decreases. This is mainly attributed to several phenomena such as: concentration polarisation, membrane fouling, osmotic pressure,

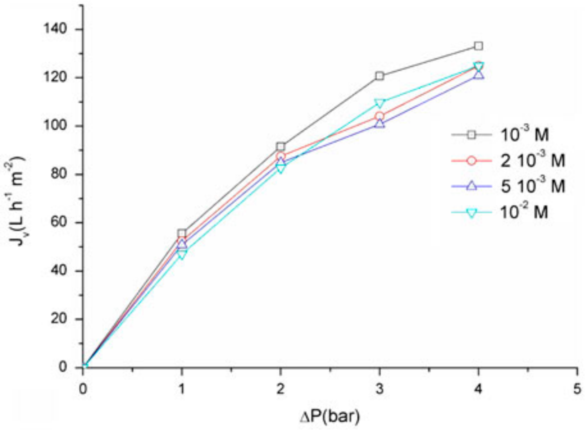

Fig. 4b. Permeate flux as a function of transmembrane pressure at different PAA concentrations, $[Cu^{2+}] = 10^{-3}$ mol L^{-1}.

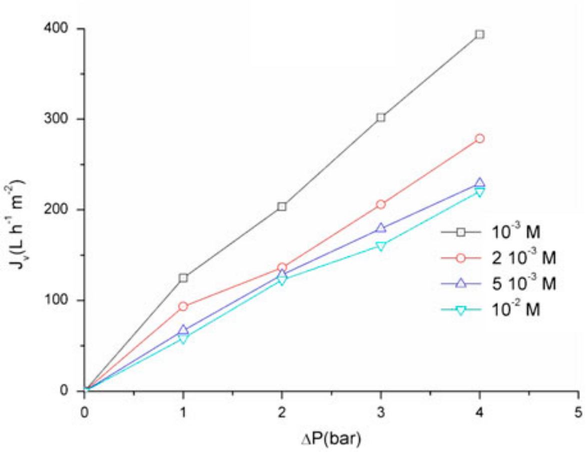

Fig. 4c. Permeate flux as a function of transmembrane pressure at different PAA concentrations, $[Zn^{2+}] = 10^{-3}$ mol L^{-1}.

precipitation and formation of gel layer on the membrane's surface.

The analysis of both figures calls for caution not to exceed 3 bar in transmembrane pressure, otherwise metal ions retention would be endangered and concentration polarization would be enhanced.

3.4. Effect of pH

Heavy metals are known to exist as free ions in a strong acidic medium. At these conditions their molecular sizes are less than the pore sizes of UF membranes and they freely pass through the membranes. Since, pH sensitivities of metal–polymer complex formation vary significantly from metal to metal; this can be exploited for their selective separation.

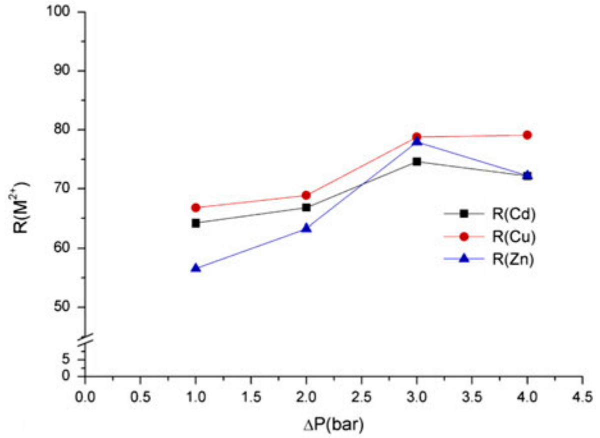

Fig. 5. Heavy metal retention as a function of transmembrane pressure, $[M^{2+}] = 10^{-3}$ mol L^{-1}, $[PAA] = 2 \times 10^{-3}$ mol L^{-1}.

The effect of pH on copper, cadmium and zinc retention was investigated in the range 1.0–9.0, the concentrations of PAA and heavy metals have been taken as 2×10^{-3} mol L^{-1} and 10^{-3} mol L^{-1}, respectively, and transmembrane pressure of 3 bar.

Fig. 6(a) describes the pH effect on the retention of heavy metals. It shows, at low pH, retention of metal ions decreases. This is due to a competition of hydrogen ions with cadmium, copper and zinc trapped in the PAA structure. The carboxylic functional groups (COOH) of polymer would not be dissociated and the PAA chain forms highly compact clusters, which are joined by short extended parts of a polymer chain whose microenvironment polarity is identical with that of hydrophobic areas of PAA.

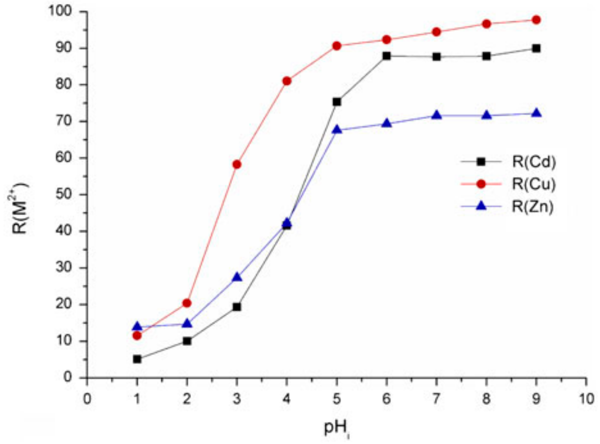

Fig. 6. Heavy metal retention as a function of initial pH, $[M^{2+}] = 10^{-3}$ mol L^{-1}, $[PAA] = 2 \times 10^{-3}$ mol L^{-1}, $\Delta P = 3$ bar.

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 [23]. Above pH 5, the removal of cadmium, copper and zinc exceeded, respectively, 80, 93 and 70%.

The charge of a membrane varies with the pH around its isoelectric point. The electrostatic effect of a membrane, which affects the retention factor, therefore varies with the pH. The membrane used in this study is a polyethersulphone active layer. For low pH value, the membrane is positively charged. In this situation, possible interactions between polymer molecules and membrane are those consisting of hydrogen bonds.

At pH above isoelectric point, the membrane is negatively charged. Associated with pH solution grows, carboxylic groups of polymer start dissociating and presence of carboxylate anions (COO^-) is more important. The existence of electrical charges in molecule provokes intramolecular and intermolecular repulsion forces. This fact means expansion of chain, acquisition of a rod-like structure [24] and the lack of aggregation between polymer molecules.

3.5. Ultrafiltration of mixture metal ions solution

In order to study the selective complexation of a specific metal in presence of other metals and then his separation in the same conditions, a solution containing Cd (II), Cu (II) and Zn (II) was adjusted at pH 5 and ultrafiltrated at a fixed transmembrane pressure at 3 bar and varied PAA concentrations.

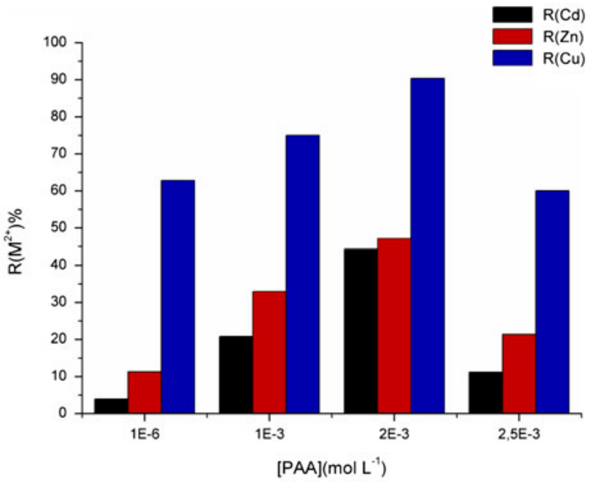

Fig. 7. Heavy metal retention of ions in a mixture solution, $[M^{2+}] = 10^{-3}$ mol L^{-1}, $[PAA] = 2 \times 10^{-3}$ mol L^{-1}, $\Delta P = 3$ bar, pH = 5.

Table 1
Values of complex formation constant at 25˚C [27,28]

Ion métallique	Cd(II)	Cu(II)	Zn(II)
K_c at 25˚C	7.94×10^2	1.58×10^{11}	2.24×10^9

Fig. 7 illustrates the variation of heavy metal retention as a function of PAA concentrations at a fixed heavy metal ions concentration of 10^{-3} mol L^{-1}. The results show for all PAA concentrations, copper retention is higher than cadmium and zinc. The metal ion retention decrease in the following order: Cu(II)>Zn (II)>Cd(II).

Higher Cu(II) rejection in comparison with Cd(II) and Zn(II) can be explained by the formation of more stable complex with PAA than Zinc and Cadmium as shown in Table 1.

The decrease in the Cd retention could be attributed to its ionic radius and its ionic radius which are greater than those of Cu and Zn. In fact, the ionic radius of cations $Cd^{2+,}$ Cu^{2+} and Zn^{2+} are, respectively, 97, 72 and 74 pm [25]. Tansel et al. [26] reported that ions with lower ionic radius tend to hold their hydration shell and are strongly attached to water molecules, thus would be more removed by membrane.

4. Conclusion

In this paper, enhanced ultrafiltration by the addition of poly(acrylic acid), with an average molecular weight (100 kDa), for the removal of Cu(II), Cd(II) and Zn(II) from aqueous solutions has been studied.

In the absence of PAA, rejection of free metal ions Cd(II), Cu(II) and Zn(II) are low and they do, respectively not exceed 4, 6 and 10%. In the presence of PAA, heavy metals retention increases with the increase of transmembrane pressure and PAA concentrations until to 2×10^{-3} mol L^{-1}. Retention rises and reaches 75, 80 and 77% for cadmium, copper and zinc, respectively. A best retention was observed at 3 bars.

The variation of permeate flux as a function of the transmembrane pressure for different feed concentrations of PAA were studied. It showed that the permeate flux increases with transmembrane pressure and decreases with the increase of polyelectrolyte concentration, insignificant polarization concentration phenomenon, fouling and increase of solvent viscosity were observed.

The pH effect study on the heavy metal ions recovery revealed a maximum retention around 80, 93 and 70% cadmium, copper and zinc, respectively, for pH 5. In mixture solution, copper retention is higher than cadmium and zinc for all PAA concentrations.

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