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Chelating water-soluble polymers associated with ultrafiltration membranes for metal ion removal

Bernabé L. Rivas · Sara Hube · Julio Sánchez · Eduardo Pereira

Abstract This article describes the retention properties of commercial chelating water-soluble polymers, for different metal ions in aqueous solution using a liquid-phase polymer-based retention (LPR) technique. The polymers studied were poly(ethyleneimine) or P(EI) (water-free and a 50 % aqueous solution) and poly(ethyleneimine epichlorohydrin) or P(EIE) (a 17 % aqueous solution). These commercial polymers were fractionated by ultrafiltration membranes and then characterized by Fourier-transformed infrared spectroscopy. The extraction process was performed using the following metal ions: Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+}. In the washing studies, we varied the pH (3, 5 and 7) and retention time. The results showed that P(EI) showed high retention for all the metal ions at pH 7 and for selective retention of Cu^{2+} at pH 5, while P(EIE) showed selective retention of Cu^{2+} ions at pH 7. Using the enrichment method, the maximum retention capacity of Cu^{2+} and Cd^{2+} was achieved using a 50 % aqueous solution of P(EI) at pH 5 and 7, respectively. Finally, charge–discharge experiments for Cu^{2+} were analysed by changing the pH from basic to acidic over three cycles. These results showed that it is possible to remove metal ions and regenerate the removal capacity of the polychelatogens using the LPR technique.

Keywords Chelating water-soluble polymers · Metal ions · Membranes · Ultrafiltration

Introduction

Functional polymers play a special role in material science and technology because they offer several paths for new applications in environmental science, industrial separation processes and biological research.

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Polychelatogens and polyelectrolytes are two examples of functional polymers. Polychelatogens, or chelating polymers, can be distinguished from polyelectrolytes because they have functional groups capable of forming chemical bonds with metal ions in solution, whereas polyelectrolytes have charged functional groups, or are easily ionized in aqueous solution, and mainly interact by ion exchange.

A typical procedure used to synthesize functional polymers involves free-radical polymerization. With a choice of appropriate monomers, it is possible to generate a polymer with certain characteristics such as water solubility, ability to bind metal ions and selectivity [1, 2]. These macromolecules can be homo- or copolymers, and they possess one or more functional groups in the chain. The most studied ligands in the case of polychelatogens are amines, carboxylic acids, amides, alcohols, amino acids, pyridines, thioureas and imines [3].

A large number of water-soluble functional polymers have the capacity to separate ions in solution through a membrane. This hybrid complexation–ultrafiltration technique is also known as polymer-assisted ultrafiltration, or liquid-phase polymer-based retention (LPR). This technique involves the use of an ultrafiltration membrane that separates the low molecular weight ionic species interacting with the functional groups of the water-soluble polymers from species with high molecular weights by preventing them from passing through the membrane [1–10]. In the LPR experiments, high molecular weight polymers are used in combination with membranes with a low exclusion limit to assure that the macromolecule remains in the feed phase.

The most important physical properties of these membranes include interfacial tension and interfacial adsorption. In this context, van der Waals interactions, hydrogen bonds, electrostatic effects, charge transfer interactions and dipole interactions all play a critical role in the function of the membrane [5]. The membranes are usually made up of polycarbonate or cellulose esters, polyamides and polysulphones [1].

Different types of separation can be performed using the LPR technique. In the washing method, the solution containing the ionic species and the polymer is placed into the cell and is ultrafiltrated by eluting with pure solvent. This method is similar to diafiltration, or the batch method. In the enrichment method, the polymer solution is placed inside the cell and filtered, creating a flow through the cell containing ionic species in solution [6–8]. Using the enrichment method, the maximum retention capacity (MRC) of the polymer can be determined.

The great advantage of LPR is the homogeneous nature of the technique. Thus, it largely avoids the phenomenon of mass transfer, or diffusion, which is limiting in heterogeneous methods [5]. Also, the energy requirement for LPR is low.

This study is focused on the use of commercial, functional, water-soluble polymers, such as poly(ethyleneimine), P(EI) (water-free and 50 % aqueous solution) and poly(ethyleneimine epichlorohydrin), P(EIE) (17 % aqueous solution) to remove metal ions from aqueous solutions. Before the removal process, these commercial polymers were first fractionated using ultrafiltration membranes and characterized by Fourier-transformed infrared (FTIR) spectroscopy.

The LPR technique was performed using a solution containing Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+}. The variables studied for the washing method included pH and retention time.

The MRC was determined for each polymer at the optimum pH using the enrichment method. After MRC, the new polymer–metal complex obtained was also characterized using FTIR spectroscopy.

Finally, retention–elution experiments for Cu^{2+} were analysed by changing the pH from basic to acidic over of three cycles.

Experimental

Reagents and apparatus

The commercial polychelatogens poly(ethyleneimine) (P(EI), Aldrich, Milwaukee, WI) and poly(ethyleneimine epichlorohydrin) (P(EIE), Aldrich) were purified and fractionated using 10 kDa polyethersulphone ultrafiltration membranes (Millipore). The polychelatogen structures are shown in Fig. 1.

Analytical-grade metal nitrates of Ni^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+} and Zn^{2+} (Merck, Stuttgart, Germany) were used as received. The solutions were prepared with twice-distilled water. The concentrations of metal ions (in mg L^{-1}) in the ionic solution were 14.5 (Ni^{2+}), 28 (Cd^{2+}), 14.5 (Co^{2+}), 16 (Cu^{2+}), 13 (Cr^{3+}), 52 (Pb^{2+}) and 16.5 (Zn^{2+}). HNO_3 (J.T. Backer), HCl (Fisher), NaOH pellets (Aldrich) and liquid nitrogen (AGA) were used as received.

A Unicam Solaar M5 atomic absorption spectrometer (Unicam, UK) was used for the determination of the metal ion concentrations. Solution pH was determined using a Digital inoLab WTW pH metre.

Fig. 1 Structures of the polychelatogens: **a** P(EI) and **b** P(EIE)
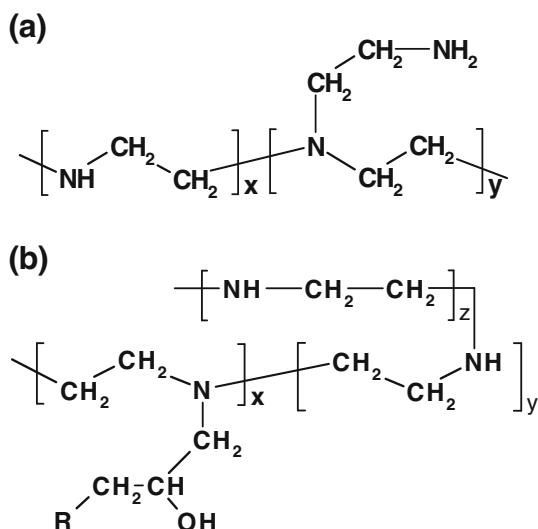
FTIR spectroscopy

Characterization of commercial polymers and polymer–metal complexes was carried out by FTIR spectroscopy. FTIR was performed using Magna Nicolet 550 and Nexus Nicolet spectrometers. For the quantitative analysis, 1 mg of the sample per 100 mg of KBr was employed.

The FTIR studies were performed over the range of 400–4,000 cm^{-1}. The main characteristic absorption bands (in cm^{-1}) in the polymers include the following:

P(EI): 3359.87, 1647.83 (N−H); 1466.99, 767.40 (−CH$_2$−); 1311.18 (C−N).
P(EIE): 3422.44 (OH, N−H); 1630.59 (N−H); 1384.10 (C−N).

Ultrafiltration procedure

When a polychelatogen and metal ions are placed in contact and diafiltered through the ultrafiltration membranes, metal ions that interact strongly with the polychelatogens are retained, whereas metal ions with low interaction strengths are eluted through the membrane in the permeate stream. Therefore, the ions retained by the functional polymer do not pass through the membrane.

The main features of the LPR system (Amicon) include a filtration cell with a magnetic stirrer containing a filtration membrane composed of polyethersulphone with a known exclusion (10 kDa) rating, and a reservoir and a pressure source (nitrogen bottle). The LPR equipment was previously described elsewhere [1, 5].

In LPR, two kinds of experiments can be performed. The first one is a *washing method*, which is an elution method based in continuous diafiltration by addition of solvent at a constant volume. Before carrying out the ultrafiltration, the pH of the ionic solution was adjusted. The resulting polymer/metal ion mixture was stirred for 1 h at room temperature, and then placed in the ultrafiltration cell. The solution was submitted to ultrafiltration and washed with twice-distilled water at the same pH. Ultrafiltration was performed under a total pressure of 3.5 bar using an ultrafiltration membrane composed of polyethersulphone, with a molecular mass cut-off of 10 kDa. The total cell volume was kept constant during the filtration process.

To use the washing method, two factors needed to be defined (Eq. 1) to determine the polymer's retention capacity for metal ions from the solution: (1) retention (*R*) and (2) filtration factor (*Z*).

$$R(Z) = \frac{C^{\text{free}}(Z) + C^{\text{bound}}(Z)}{C^{\text{initial}}} \tag{1}$$

where C^{free} is the absolute amount of metal ions that are free in the solution, C^{bound} is the absolute amount of metal ions that are bound to the polymer and C^{initial} is the absolute amount of metal ions at the start of the experiment. The filtration factor (*Z*) is the ratio between the total permeate volume (V_{f}) and the retentate volume (V_{o}):

$$Z = V_{\text{f}} / V_{\text{o}} \tag{2}$$

Using the experimental data, a graph (a retention profile), in which *R* is represented as a function of *Z*, can be drawn.

The second mode used in LPR is *the enrichment method*, which is a concentration method based on continuous diafiltration by addition of solvent and metal ions at a constant volume. This method is used to determine the MRC of the polychelatogen. A solution containing the metal ions is passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both the cell and reservoir solutions were adjusted to the same pH. In both the washing and enrichment methods, a blank experiment (in the absence of the polychelatogen) was necessary to evaluate the interaction of the membrane with metal ions.

In the charge–discharge process, the enrichment and washing methods were alternately used at basic and acidic pHs, respectively.

Results and discussion

Removal of metal ions by the washing method

Effect of pH on metal ion removal

It is well known that polyamines such as P(EI) are suitable macromolecular ligands for complexation–ultrafiltration of metal ions [11–15]. P(EI) possesses a number of advantages as a polymer-chelating reagent, including high water solubility, a high concentration of functional groups, good physical and chemical stability, and a suitable molecular weight [11].

In general, our results on the effect of pH on metal ion removal show that when the pH is increased, the retention capacity for metal ions is also increased.

In the case of P(EI) (water-free) at pH 3, the retention capacity was null for all the metal ions studied, except for Cu^{2+}, which showed a 38 % removal efficiency (see Fig. 2a). At pH 5, the retention capacity of P(EI) (water-free) was selective for Cu^{2+} approaching 84 % removal efficiency and below 20 % for the other metal ions studied (see Fig. 2b). The presence of different amino groups in the polymer structure allowed for an effective interaction–retention of all metal ions at pH 7 (see Fig. 2c) (Cd^{2+} 97 %, Zn^{2+} 95 %, Cu^{2+} 100 %, Co^{2+} 100 % and Ni^{2+} 100 %), with the exception of Pb^{2+} and Cr^{3+}.

The results of the polymer–metal ion interaction for P(EI) (50 % aqueous solution) were as follows: at pH 3, the P(EI) (50 % aqueous solution) presented selectivity only for Cu^{2+}, reaching 74 % retention (see Fig. 3a). At pH 5, the retention of all the metal ions increased, especially for Cu^{2+}, which reached 100 % (see Fig. 3b). At pH 7, the retention capacity for all metal ions was maximized (Cd^{2+} 99 %, Zn^{2+} 98 %, Cu^{2+} 100 %, Co^{2+} 98 % and Ni^{2+} 100 %), with the exception of Pb^{2+} and Cr^{3+}, which showed no retention (see Fig. 3c).

P(EI) showed the highest metal retention capacities at higher pH values, where the amine groups were more available and could coordinate more easily with the metal ions. Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} have similar ionic radii and unfilled *d*-orbitals, which are necessary for bond formation with the electron pair of the amine groups in the polymers. However, Pb^{2+} and Cr^{3+} have more stable electronic structures, preventing complex formation [11].
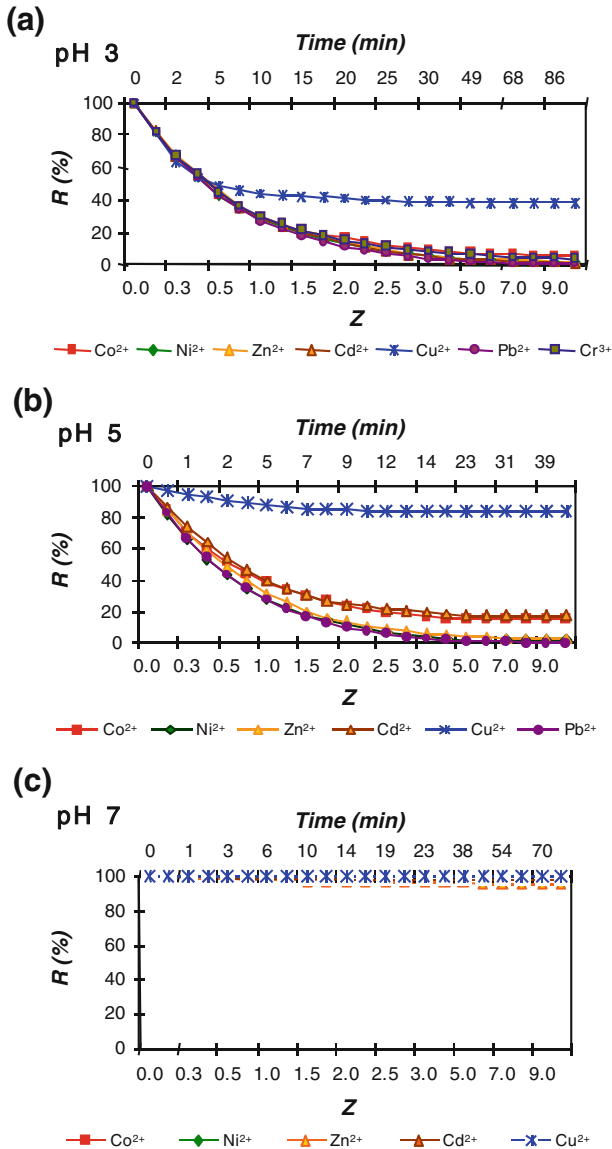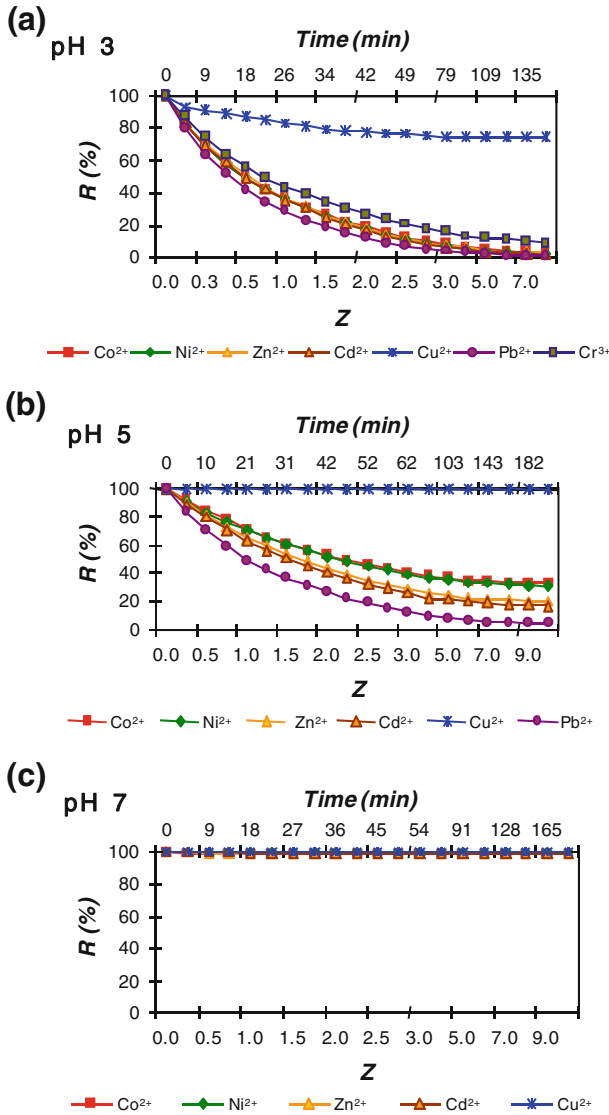
Fig. 2 Retention profiles of metal ions at **a** pH 3, **b** pH 5, and **c** pH 7 as a function of Z and time, using P(EI) water-free

The retention capacity of P(EIE) (17 % aqueous solution) was lower compared with P(EI) for all the metal ions studied. The retention profiles obtained for this polychelatogen at pH 3 showed negligible retention capacity for all the metal ions studied (see Fig. 4a). At pH 5, the retention was lower than 10 % for all the metal ions, but it was 34 % in the case of Cu^{2+} (see Fig. 4b). High selectivity for Cu^{2+}

Fig. 3 Retention profiles of metal ions at **a** pH 3, **b** pH 5, and **c** pH 7 as a function of Z and time, using P(EI) 50 % aqueous solution

was observed at pH 7, reaching 100 % retention (see Fig. 4c), while all other ions showed retention values below 40 %.

P(EIE) showed lower metal ion retention compared with P(EI) likely because of the presence of hydroxyl groups in its polymeric structure, which are weaker ligands than amine groups, thereby reducing the metal ion binding capacity in P(EIE). In addition, the presence of hydroxyl groups reduced the number of amine ligands per
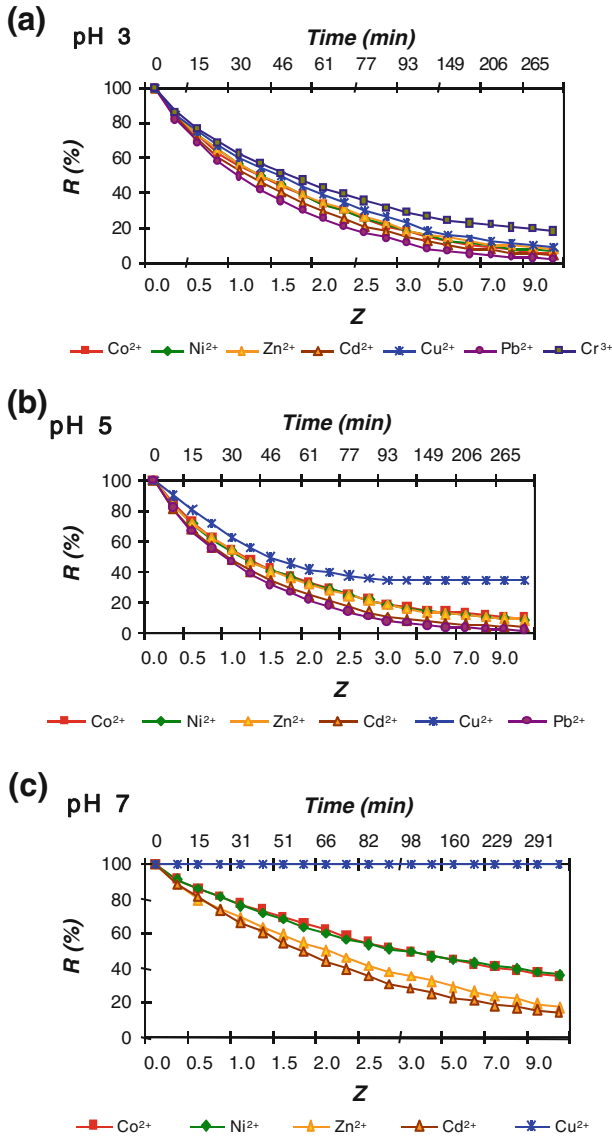
(a)

(b)

(c)

Fig. 4 Retention profiles of metal ions at **a** pH 3, **b** pH 5 and **c** pH 7 as a function of Z and time, using P(EIE) 17 % aqueous solution

mass unit and increased the steric hindrance, preventing complex formation in many cases [11].

The main results regarding the influence of pH on metal ion removal by polychelatogens studied at $Z = 10$ are summarized in Fig. 5. The highest retention capacity for metal ions is observed at pH 7. Complexation occurs mainly when the polychelatogen is in the unprotonated form, containing available lone pairs on the nitrogen atoms that can react with the metal ions in the solution. Acid–base and

Fig. 5 Metal ion removal by the washing method at $Z = 10$, using **a** P(EI) water-free, **b** P(EI) 50 % aqueous solution and **c** P(EIE) 17 % aqueous solution
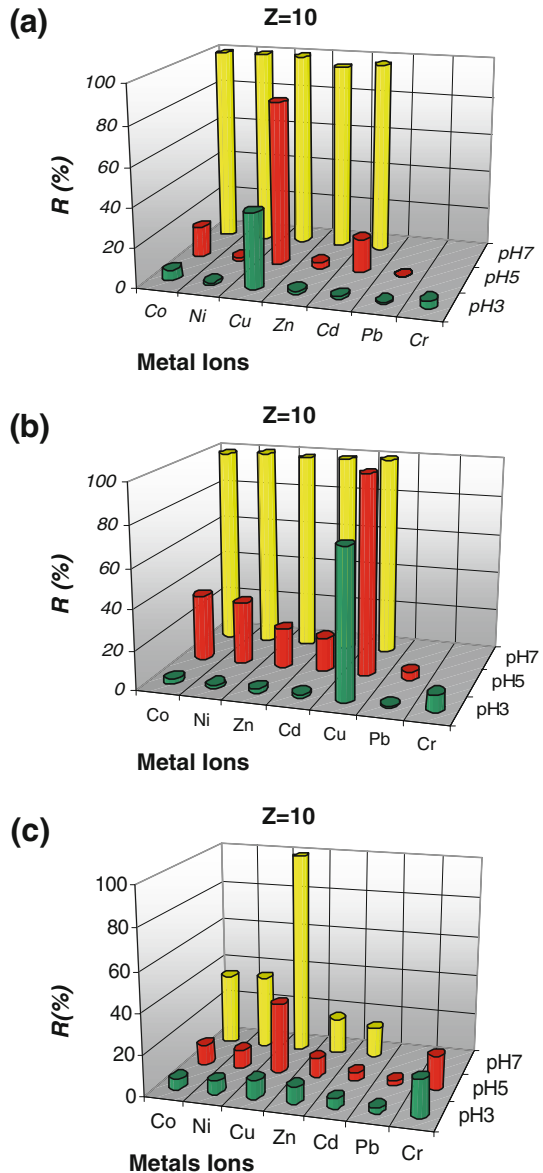
complexation equilibria are competitive in the polymer depending on the pH conditions; at more basic pHs, the polymer can complex the metal ions or under more acidic conditions, remain in aqueous solution in its protonated form [15].

The selectivity of the polychelatogens may be understood through the HSAB Pearson's Principle. This principle states that hard acids prefer to bind hard bases and that soft acids prefer soft bases [16]. Based on this principle, amine groups are interpreted as hard bases; therefore, they show a higher interaction with

hard acids and with those that are on the borderline between hard and soft (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}). However, Irving and Williams [17] established the order of stability of bivalent transition metal complexes as $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} \ll Cu^{2+} > Zn^{2+}$. This is an empirical rule that could explain the selectivity of polychelatogens towards Cu^{2+} ions based on higher complex stability.

Study of ultrafiltration time

The ultrafiltration time was analysed at each pH using the washing method with the polychelatogens under the previously established conditions.

In the case of P(EI) water-free, the ultrafiltration reached $Z = 10$ after 86, 39 and 70 min at pHs 3, 5 and 7, respectively. For P(EI) (50 % aqueous solution), the ultrafiltration reached $Z = 10$ after 135, 182 and 165 min for pHs 3, 5 and 7, respectively. For P(EIE) (17 % aqueous solution), the ultrafiltration times to reach $Z = 10$ were 265, 205 and 291 min for pHs 3, 5, and 7, respectively. The maximum time required for the ultrafiltration at $Z = 10$ was observed using polymers that came from aqueous solution: P(EI) (50 % aqueous solution) and P(EIE) (17 % aqueous solution). The difference in ultrafiltration times using different polymers can be explained by the combined effects of conformational changes, size and hydrophilicity of the polychelatogen in solution, as well as effects characteristic of the adsorbed polymer layers and metal ions on the polyethersulphone membrane, which may result in fouling effects [18].

We also monitored the Z factor as a function of ultrafiltration time. For P(EI) (water-free), the results indicate that Z varies as a function of ultrafiltration time following a positive linear trend (Fig. 6a). The correlation factor (r^2) was 0.988, 0.988 and 0.987 at pHs 3, 5 and 7, respectively.

In the case of P(EI) (50 % aqueous solution) (see Fig. 6b), this correlation was also linear, and the r^2 values were 0.998, 0.999 and 0.999 at pHs 3, 5 and 7, respectively.

Finally, for P(EIE) (17 % aqueous solution) (see Fig. 6c), this correlation was also linear, and the r^2 values were 0.999, 0.998 and 0.999 at pHs 3, 5 and 7, respectively. Analysing these parameters, we can obtain information to help predict the ultrafiltration time needed under different conditions.

MRC of metal ions using the enrichment method

The MRC of metal ions by the polychelatogen was determined using the enrichment method. The MRC is defined as follows:

$$MRC = (M\,V)/Pm \tag{3}$$

where M is the initial concentration of metal ions (mg L^{-1}), V is the volume of filtrate (volume set) containing the metal ions (mL) that passes through the membrane and Pm is the amount of polymer (g). The MRC of metal ions was calculated using the total volume of filtrate (300 mL).

Due to the complex equilibria between the polymer and metal ions, a low rate of increase for the metal ion concentration in the filtrate is normally expected. From
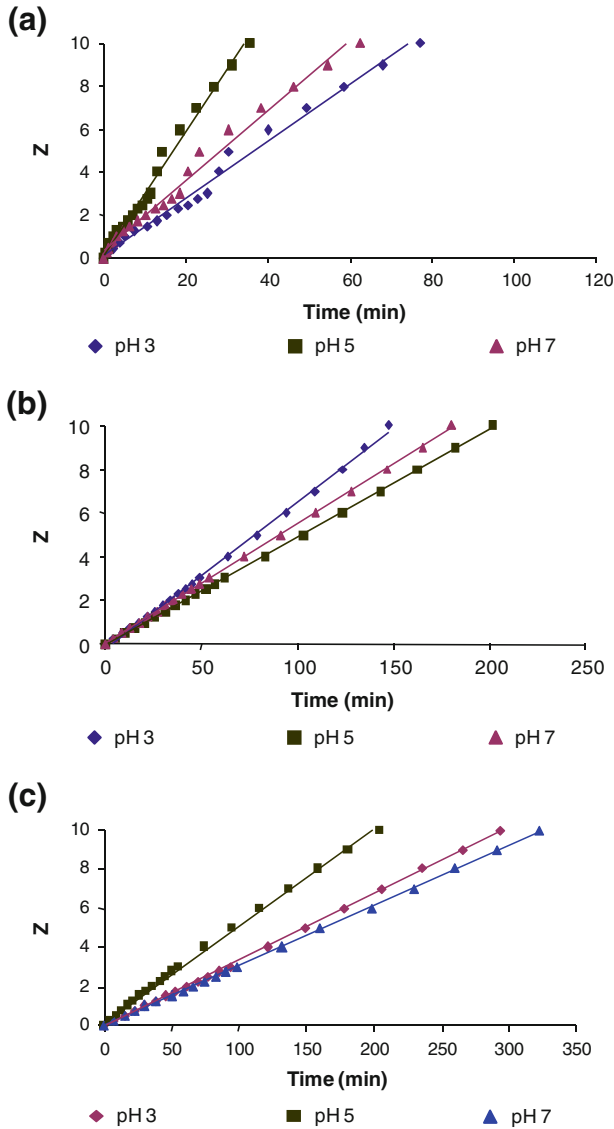
Fig. 6 Profile of Z as a function of ultrafiltration time using the washing method at different pH values up to $Z = 10$, using **a** P(EI) water-free, **b** P(EI) 50 % aqueous solution and **c** P(EIE) 17 % aqueous solution

the difference in the slopes, the amount of metal ions bound to the polymer, free in solution, and the MRC can be easily calculated [1, 5].

The enrichment experiments were performed using P(EI) (water-free) and P(EI) (50 % aqueous solution) by analysing Cu^{2+} at pH 5, and Cd^{2+} and Co^{2+} at pH 7 in separate experiments.

The maximum retention of Co^{2+} was obtained using P(EI) water-free at pH 7 (see Fig. 7).

The highest retention of Cu^{2+} and Cd^{2+} was found for P(EI) (50 % aqueous solution) at pH 5 and 7, respectively (see Fig. 8).

This behaviour was similar to the results observed in the washing method, showing efficient capacity to remove Cu^{2+} at pH 5, where the amine groups were more available and could coordinate more easily with the metal ions. The maximum retention capacities for both polymers are summarized in Table 1.

FTIR spectroscopy of polymer–metal ion

The FTIR spectra of P(EI) (50 % aqueous solution) before and after reaching the MRC for Cu^{2+}, Co^{2+} and Cd^{2+} are shown in Fig. 9.
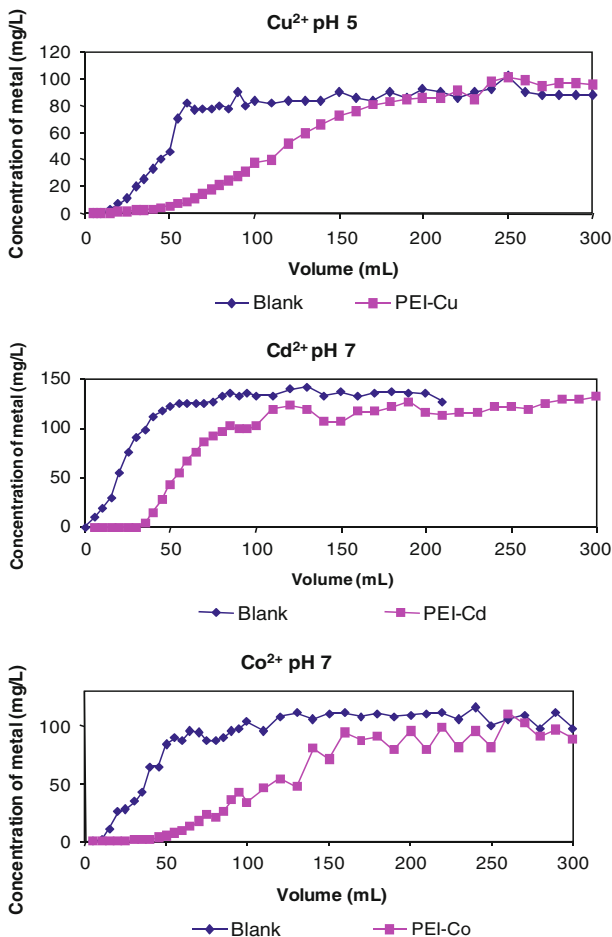

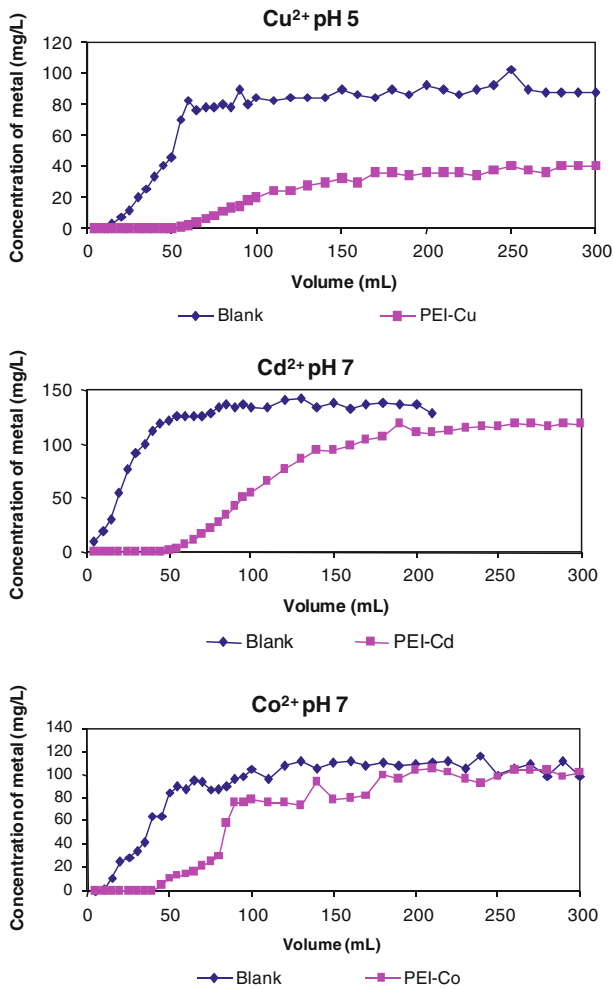Fig. 7 MRC of Cu^{2+} at pH 5, Cd^{2+} and Co^{2+} at pH 7 by P(EI) water-free

Fig. 8 MRC of Cu^{2+} at pH 5, Cd^{2+} and Co^{2+} at pH 7 by P(EI) 50 % aqueous solution

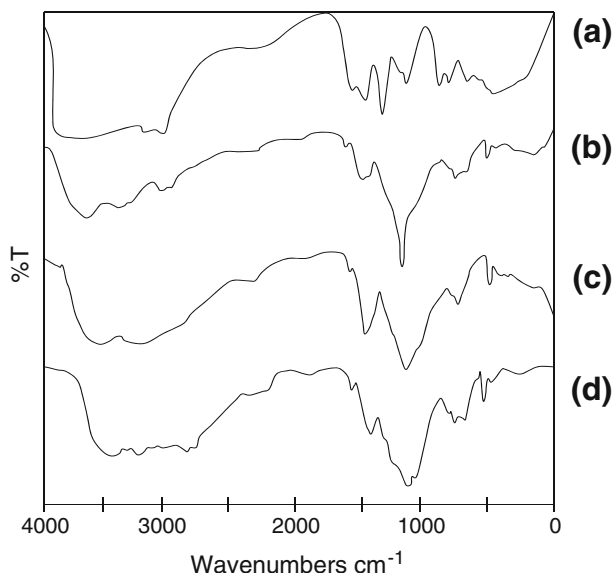|	Metal ions	MRC (mg metal ion g^{-1} polymer)	MRC (mol metal ion g^{-1} polymer)
Table 1 MRC at pH 7 of Cu^{2+}, Cd^{2+} and Co^{2+} of P(EI) water-free and P(EI) 50 % aqueous solution			
	P(EI) water-free		
	Cu^{2+}	211	0.140
	Cd^{2+}	202	0.075
	Co^{2+}	192	0.136
	P(EI) 50 % aqueous solution		
	Cu^{2+}	375	0.246
	Cd^{2+}	509	0.189
	Co^{2+}	141	0.099

Fig. 9 FTIR spectra of P(EI) (50 % aqueous solution) before (*a*) and after the MRC of (*b*) Cu^{2+}, (*c*) Co^{2+} and (*d*) Cd^{2+}

In the high frequency region of the spectra, only vibrations of functional groups corresponding to P(EI) could be identified. Some modifications were observed in the spectra in the $1,700$–$1,300$ cm^{-1} range.

The polymer–metal complex obtained shows new band intensity at $\sim 1,380$ cm^{-1} for Cu^{2+} and Co^{2+}, and at $\sim 1,350$ cm^{-1} for Cd^{2+} [19, 20]. This absorption band correlates with a displacement of the characteristic C–N band that is present in the polymer spectra. This can be attributed to complex formation between the polymer and the metal ion. Moreover, the spectrum shows new bands at ~ 820 cm^{-1}, supporting the presence of metal ions in the polymer.

The charge–discharge process

Once the polychelatogen becomes exhausted (charge), the metal ion must be recovered, regenerating the polychelatogen. A successful desorption process (discharge) must restore the polymer close to its initial state for effective reuse. We named this process as charge–discharge.

In the charge–discharge process, the enrichment method was alternately used with the washing method by changing the pH from basic to acidic in the reservoir. This process was repeated three times for each polymer to determine its capacity for metal ion delivery and to regenerate the binding ability of the polychelatogen.

This study was conducted with P(EI) water-free, P(EI) (50 % aqueous solution) and Cu^{2+}. The molar ratio polymer to metal ion used was 40:1. The charging of the polychelatogen with Cu^{2+} was performed at pH 7.

To fully discharge the spent polymer, the first step in this process was the choice of the better eluent (acid). The acids used in this part were HCl and HNO_3 (0.05 and 0.1 N, respectively).

The results show higher elution capacity at $Z = 10$ using higher concentrations of acid. For P(EI) water-free, the best condition was found using 0.1 N HCl and HNO_3 (93 %) (see Fig. 10a). However, when P(EI) 50 % aqueous solution was used as the sequestration agent, the subsequent elution capacity at $Z = 10$ was maximized (95 %) with HNO_3 as compared with HCl at the same concentration (0.1 N) (see Fig. 10b). Therefore, the best eluent for the charge–discharge process was determined to be 0.1 N HNO_3.

Figure 11 shows the charge–discharge behaviour for Cu^{2+} using P(EI) water-free and P(EI) (50 % aqueous solution). This procedure was performed in triplicate.

The first step was the charge (C1) of the polychelatogens with Cu^{2+} using the enrichment method at pH 7. This first charge of Cu^{2+} was performed in order to reach 100 % retention under the optimum conditions for both polymers. The charge was performed with a total of 300 mL of solution in the presence of interfering ions in the ultrafiltration cell with the reservoir at constant volume (20 mL).
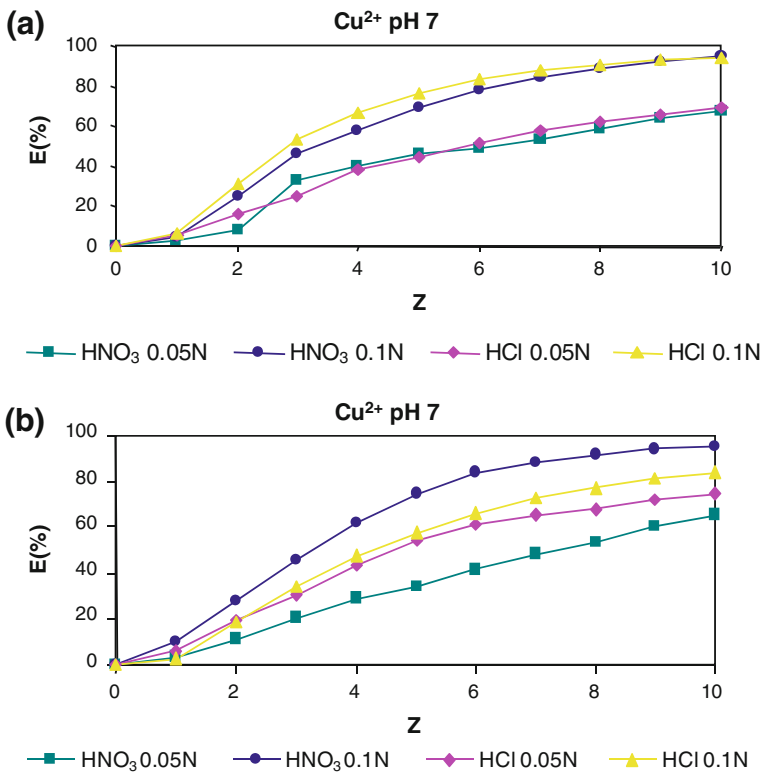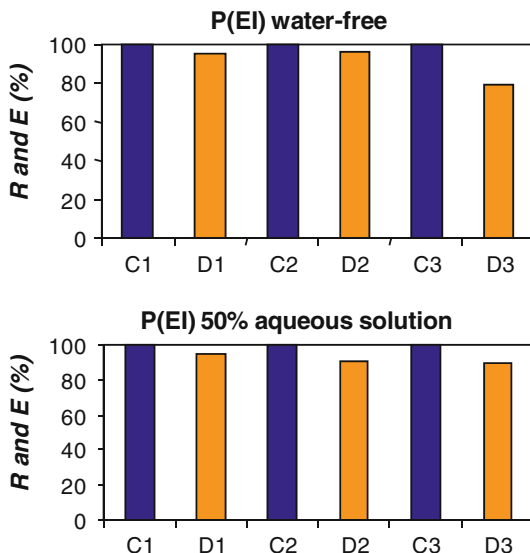

Fig. 10 Elution profiles for Cu^{2+} as a function of Z for **a** P(EI) water-free and **b** P(EI) 50 % aqueous solution

After the first charge (C1), the discharge (D1) was performed using the polymer–Cu^{2+} composite. This solution was washed into ultrafiltration cell with reservoir water buffered at an acidic pH using the washing method with 0.1 N HNO_3.

The first discharge (D1) of Cu^{2+} was effective for both polymers. The elution process recovered 90 % of Cu^{2+} retained by the polymer during the charge process.

The second charge (C2) at pH 7 reached the polymers' MRC when compared with the first charge process (C1). The second discharge (D2) at acidic pH showed almost the same behaviour than first discharge (D1) for P(EI) water-free, releasing greater amounts of Cu^{2+} ions into the filtrate. The third charge (C3) at pH 7 was effective for both the polymers, compared with the second one (C2).

Finally, the third discharge (D3) of Cu^{2+} from the polymer at acidic pH was lower compared with D2 but still released approximately 80 % of the Cu^{2+} ions.

Conclusions

This investigation pursued the retention properties of different metal ions from water using P(EI), and P(EIE), using a polymer-assisted ultrafiltration technique.

The variables studied using the polymer-assisted ultrafiltration with the washing method included pH and retention time. The extraction process was performed for Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+}. In general, the results showed that when the pH increased, the retention capacity of metal ions also increased. P(EI) showed the highest metal retention capacities for all the metal ions studied at pH 7. At a basic pH, the amine groups were more available and could coordinate more easily with the metal ions. P(EI) presented selective retention of Cu^{2+} at pH 5. P(EIE) showed only a selective retention of Cu^{2+} ions at pH 7. We have also observed a difference in ultrafiltration times using different polymers. This result

could be explained by the effect of conformational changes, size and hydrophilicity of the polychelatogens. Analysing these parameters, we can obtain information to predict the ultrafiltration time under different conditions.

Using the enrichment method, the maximum retention of Co^{2+} was obtained using P(EI) (water-free) at pH 7. The maximum retention of Cu^{2+} and Cd^{2+} was found using P(EI) (50 % aqueous solution) at pHs 5 and 7, respectively. After MRC, the polymer–metal complex was analysed using FTIR spectroscopy, showing characteristic differences in the absorption bands.

Finally, the charge–discharge experiments showed that it is possible to remove Cu^{2+} metal ions from the polymer and regenerate the extracting capacity of the polychelatogens using the polymer-assisted ultrafiltration technique.

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