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Modification of the cation exchange resin properties by impregnation in polyethyleneimine solutions Application to the separation of metallic ions

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Abstract

A commercial cation exchange resin Amberlite 200 has been modified after immersion in solutions of polyethyleneimine (PEI). The kinetic of fixation of the metallic ions have been determined. The modification of the surface of the resin deals with a change in the order of the affinities of the resins towards cations. The retention is the function of the formation and the stability of the complex. The conditions of modification (pH, PEI concentration and time of immersion) have been examined and the modification was confirmed by the determination of the exchange capacities, the distribution coefficient (P) and the selectivity factors (S). The obtained results revealed the effect of PEI on the exchange properties of the resin. The pH range selected (6–8) permitted a good adherence of PEI onto the resin surface. The quantity of the adsorbed PEI was increased by raising the initial concentration and the immersion period. The exchange capacity for copper ion passed from 2.6 mmol g^{-1}, in the case of unmodified resin, to 3.9 mmol g^{-1} for the modified one.

Keywords: Selectivity; Impregnation; PEI; Chelating resin

1. Introduction

Some previous works [1–3] have been realized in the domain of the modification of the properties of the ion exchange materials in view of the improvement of their selectivity towards metallic ions which are different by the size and the valence. This improvement of the selectivity is generally obtained by immobilization on the surface of the ion exchange materials' functional groups or reagents capable to assign to the exchanger some hydrophobic, adsorbing or complexation properties.

Gel-type anion exchange resin modified by anionic polyelectrolyte, Demol N, has been used for the separation of sulphate and nitrate ions [4].

The pyrazoles, diphosphonates, guanidyl and polyketones constitute some part of a list of

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molecules which bind to the exchanger groups and can confer to the resin acidic or basic properties [5–8].

The methylenediphosphonate and ethylenediphosphonate were used by Trochimczuk [9] for the study of the separation of Ni^{2+}, Fe^{3+}, Cd^{2+} and Zn^{2+} ions. Resins with phosphonomethyl crosslinked with branched polyethyleneimine (PEI) were used for the study of the uranium recovery from seawater [10].

The purpose of this work is to study the surface modification of a cation exchange resin by adsorption of a cationic polyelectrolyte, which confers to the resin complexation properties in addition to ion exchange one. Similar work has been presented and concerns the application of electrodeposition method in order to improve selective properties of cation exchange membrane which became after modification selective to monovalent ion (H^+) more than bivalent ones (Zn^{2+} and Cd^{2+}) [11–15].

The batch technique was used all along in this work. Fixation isotherms have been plotted according to the fixation time and the stirring conditions for different modified resins. The effects of the concentration, pH, molecular weight of the polymer and the immersion period have been examined.

2. Experimental

2.1. Materials

Amberlite 200 (Aldrich–Chemie, Steinheim) is a strong cation exchange resin containing sulphonic groups covalently fixed to a polystyrene skeleton at a concentration as high as 2.8 mmol g^{-1} of dry resin. It has been found that Amberlite 200 sorbs 0.5 g of water per gram of dry resin in a wide range of conditions. It has 20–50-mesh size and it was obtained in the Na^+ form. Before using, it was washed in 0.1 M nitric acid and then with doubly distilled water for several times, filtered, left at room temperature for 1 week in order to eliminate the excess water and stored until use.

2.2. Reagents

All chemicals were of analytical reagent grade. Salt solutions were obtained by dissolving proper amounts of the appropriate solid salt. Different solutions of Li^+, K^+, Ag^+, Cu^{2+}, Cd^{2+} and Fe^{3+} of 0.015 M were prepared from Merck salt: $LiNO_3$, KNO_3, $AgNO_3$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3$ and a known small volume of water to which 2 $M{\cdot}HNO_3$ was added in small proportions. The solutions were diluted to the required volume.

2.3. Apparatus

Metal determinations were performed using a Perkin–Elmer model 2280 flame atomic absorption spectrometer. All measurements were carried out in air/acetylene flame. The operating parameters for elements were set as recommended by the manufacturer. The wavelengths for Ag, Cu, Cd and Fe analyses were 328.1, 324.8, 228.8 and 248.3 nm, respectively. A Jenwey PFP7 emission spectrophotometer was used for Li, Na and K determinations. A pH meter with a combined electrode (Hanna Instrument) was employed for measuring pH values.

A Radiometer Tim 900 (Copenhagen) was used for the analytical study of PEI (acid–base titration, protonation ratio, pK_a).

2.4. Polyethyleneimine

PEI, a positively charged polyelectrolyte, was used as adsorbate under experimental conditions. Previous works have established that PEI and porous materials can constitute a model system to investigate the relationship between diffusion into porous structure, adsorption rate, and molecular weight of the polymer. PEI is a typical polymeric amine having chelating properties with various metal ions. It is known to exist as a linear structure or a branched structure. Commercial branched PEI was employed in this work depending on the polymerization process; it contains primary, secondary and tertiary amino groups in a ratio of approximately 1/4, 1/2 and 1/4, respectively [16].

PEI possesses quite a number of advantages as polymer chelating agent, such as good water solubility and suitable molecular weights. Chelating properties have been studied elsewhere [17,18]; it has been found using both potentiometric and spectrophotometric methods that PEI–Cu^{2+} ability complexes using branched form was 10 times higher than the linear form. Moreover, the stability constants obtained for PEI–Cu^{2+} complexes were higher than those obtained for other heavy metals such as Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and UO_2^{2+}.

In addition, PEI in aqueous solution behaved as an effective base and it was protonated at pH lower than 10.

2.5. Viscosity measurements

Viscosity measurements of the PEI solution were carried out in a water thermostat with an accuracy of ±0.1 °C using a calibrated Ubbelhode suspended bulb viscometer. The precision of the efflux times was ±0.3 s. Efflux time of the solvent (water) was always above 100 s. Reduced viscosity was determined using Eq. (1):

$$\frac{\eta_{sp}}{C}=\frac{t-t_0}{t_0 C} \tag{1}$$

where t and t_0 are the efflux times of the solution and the solvent, respectively.

2.6. Water content

The basic form of the resin and the modified ones were stirred in double-distilled water for 24 h, then filtered-off by suction, weighed, dried at 100 °C for 24 h and reweighed.

2.7. Determination of the resin capacity

Batch sorption procedures were applied. 0.1 g of the dry resin in stoppered glass tubes was shaken mechanically with 25 ml of the corresponding metal solution 0.015 M for 2 h. After equilibrium was reached, the remaining metal in the aqueous phase was analysed and the amount of metal ions loaded on the resin phase was calculated by mass balance. Resin capacities were expressed in millimole per gram of dry resin.

Experiments were carried out at a controlled room temperature of 20 ± 1 °C and reproducibility was verified by duplication.

2.8. Distribution coefficient and selectivity factor

Affinity of modified resins towards transition metals was determined by contacting the resin with 1.5×10^{-3} M nitrate metal solutions. The molar ratio of the terminal sulphonic groups in resin to metallic cations in solution was around 1:10 in all cases. After 2 h, the resin was separated by filtration and metallic ion concentration was determined by Perkin–Elmer 2280 AAS. Distribution coefficient, P, was calculated as the ratio of the amount of metal adsorbed by 1 g of dry resin and the amount of metal remaining in the solution after sorption.

The selectivity factor of two cations ($S_{M_1}^{M_2}$) can be calculated from the ratio of their distribution coefficients.

2.9. Modification procedure

In all modification cases, 3 g of resin was impregnated in 100 ml solution of different PEI concentrations agitated using a glass agitator conducted with an electric driving. At fixed stirring rate and constant temperature, the resin in solution was left during different immersion period from 1 to 10 days and at different pH values.

At the end of this operation, the resin was thoroughly rinsed with distilled water in order to eliminate the excess PEI and then dried at room temperature until the determination of exchange properties.

3. Results and discussion

The morphological characteristics were observed with a scanning electron microscope (SEM; Philips). The beads were coated with carbon film and their external and internal parts were observed using a 12 kV acceleration electron beam.

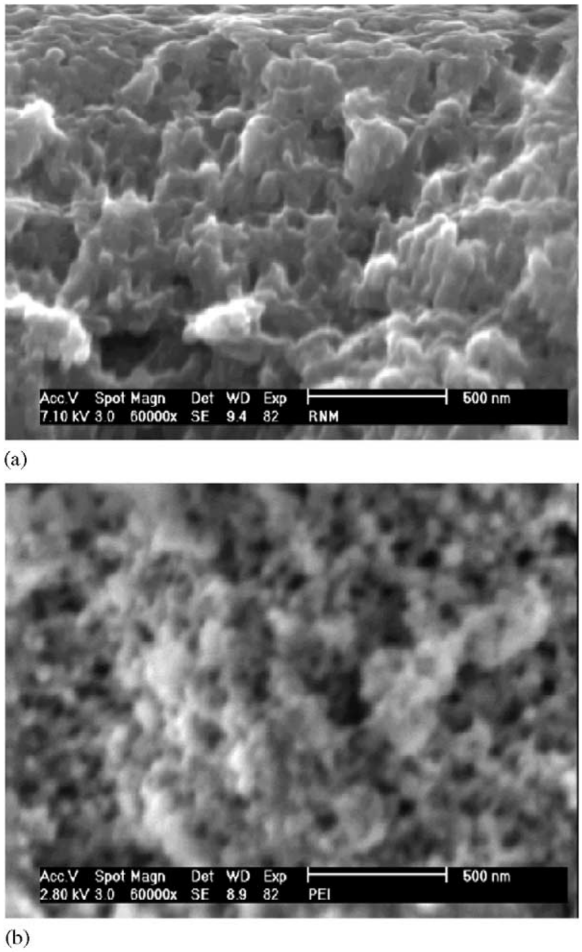

Fig. 1. SEM photographs of the surface of the Amberlite 200 resin before and after impregnation: (a) unmodified and (b) modified by impregnation in PEI 1 g l^{-1}.

The modified resin presented high surface area and low average pore diameter. The morphological features observed by SEM indicated that the modified resin presented a superficial porous structure (Fig. 1b), in contrast to the unmodified resin which has both internal and superficial pores (Fig. 1a).

3.1. Fixation of metallic ions

Fig. 2 illustrates adsorption kinetics of metallic ions on cation exchange resin unmodified (Fig. 2a) and modified with 2 g l^{-1} of PEI (Fig. 2b).

It appears that the amount of metal adsorbed increased with contact time until a plateau was obtained about 20 min for majority of the metals. During the same period of time the retention behaviour of the studied elements was different. The maximum values corresponding to the exchange capacities of the resin for ions were observed in the order: $Ag^{+} > Cu^{2+} > Cd^{2+} > K^{+} > Fe^{3+} > Li^{+}$ in the case of unmodified resin.

This order changed after modification. Impregnated resin in 2 g l^{-1} PEI solution presented a higher affinity towards transition metals than alkaline and earth alkaline elements. In the same way, affinity for copper was found superior than for other heavy metals.

As an example, ion exchange capacity ($Q = 1.76$) calculated from Cu^{2+} fixation and the distribution coefficient ($P = 0.375$) in the case of unmodified resin increased for the resin modified by PEI 50 000 ($Q = 2.81$, $P = 1.62$) and by PEI 1×10^{6} ($Q = 2.69$, $P = 1.53$). This confirmed the effective role of PEI adsorbed on the cation exchange resin surface. The molecular weight of employed PEI did not substantially affect the modification, although the Q and P values decreased slightly for the higher molecular weight.

The same order as above was obtained when 1 g l^{-1} of PEI was titrated with an equal amount of strong acid in the presence of the studied elements. Note that 1 g l^{-1} of PEI corresponded to 0.0232 mol of total nitrogen of PEI per litre of solution.

The PEI–metal complex was more stable when the titration curve of PEI, in the absence of metal, was more distant from the one of PEI in the presence of metal [19]. This means that protonated PEI changes to complex form in the presence of metal. This change was expressed by the acidity of solution which increased as a function of the stability of the complex. The stability of the complex was in the order $Cu^{2+} > Fe^{3+} > Cd^{2+}$ in agreement with the results reported in the literature [18].

3.2. Influence of the initial concentration of PEI and its structure on the resin surface

In Fig. 3 are reported the relationship between exchange capacity for Cu^{2+} and K^{+}, and the

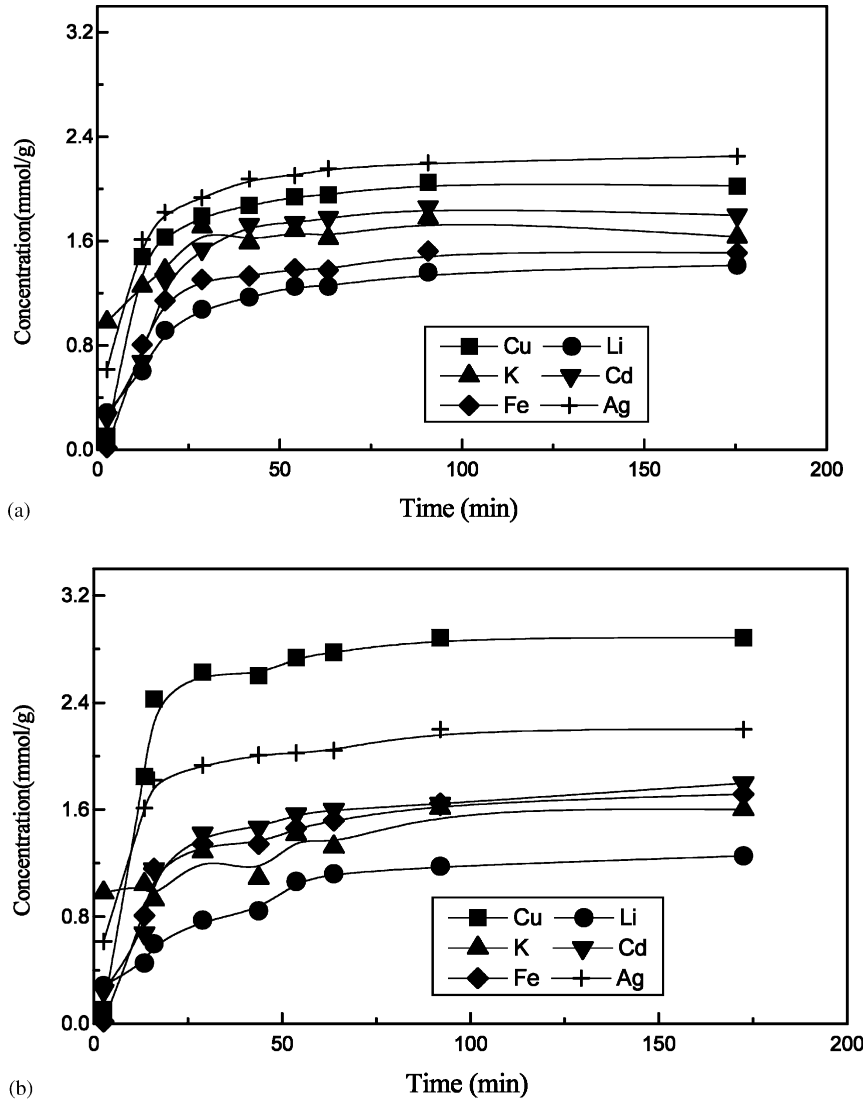

Fig. 2. Fixed amount of metallic ions on the cation exchange resin unmodified (a) and modified by PEI 2 g l^{-1}; pH 9.2; and immersion time 1 week at $T = 20$ °C (b).

amount of the adsorbed PEI on the resin at equilibrium, as a function of initial concentration of polyelectrolyte in solution in the case of modified resin. The modification parameters were chosen as follows—impregnation period: 1 week, 20 °C and constant stirring.

The amount of adsorbed PEI, at equilibrium, increased by raising the concentration of PEI and then it levelled-off. The exchange capacity for Cu^{2+} increased, while for K^{+} it was almost constant and diminished slightly with the amount of adsorbed PEI. This fact can be related to the presence of the new chelating groups on the resin. Chelation properties have a direct consequence on the fixation of transition metals such as copper and do not influence the fixation of alkaline element which do not form a complex with amine groups.

Likewise, both Cu^{2+} and K^{+} ions could be exchanged with Na^{+} of the sulphonic groups, and

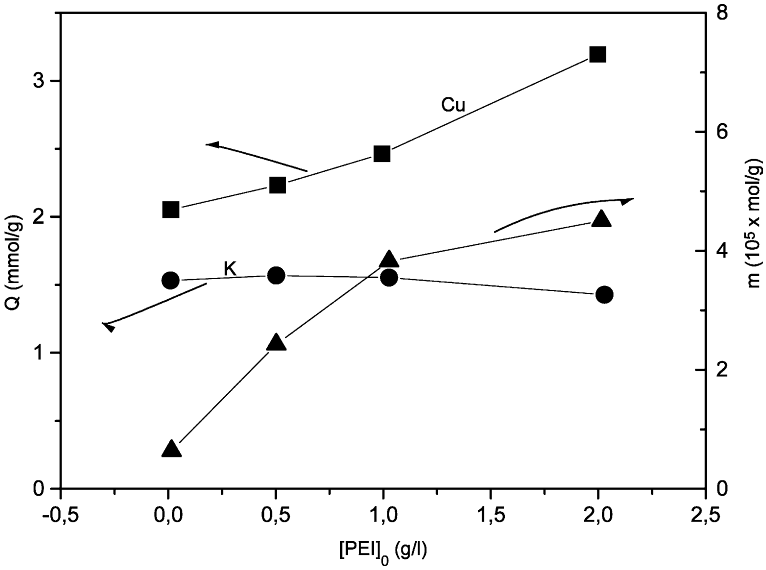

Fig. 3. Variation of Cu^{2+} and K^+ fixation as a function of initial PEI concentration. Relationship between ion exchange capacity and amount of PEI adsorbed on the cation. Immersion time 1 week at 20 °C and pH 9.8.

moreover, Cu^{2+} was linked to free amine groups by coordination bonds. These two modes of copper fixation can be described by writing the exchange equilibrium with exchanger groups and the chelate bond with amine groups as:

$$\tfrac{n}{2}Cu^{2+}(sol.) + R\text{-}(SO_3^-, Na^+)_n$$
$$\leftrightarrow nNa^+(sol.) + R\text{-}(SO_3^-, \tfrac{1}{2}Cu^{2+})_n$$

On the other hand, in the modified part of the resin, more Cu^{2+} in solution yields to:

$$xCu^{2+}(sol.) + R'\text{-}(L_4)_x \leftrightarrow R'\text{-}(L_4\text{-}Cu^{2+})_x,$$
$$R' = R\text{-}(SO_3^-, \tfrac{1}{2}Cu^{2+})_n$$

where L is the amino group and R the resin matrix.

Parallel works have been performed in order to establish the nature of the complex formed between copper ion and PEI in aqueous solution. The result obtained from the continuous variation method based on characterization of PEI–Cu^{2+} complex using spectrophotometric absorption at fixed wavelength ($\lambda_{max} = 630$ nm) for different PEI/Cu^{2+} ratio revealed that a maximum was obtained in the ratio of 4, indicating that PEI formed the most stable complex with Cu^{2+} having four coordinating amino groups. The number of amino groups was strongly related to the pH of the aqueous solution, being lower at low pH values.

Therefore, at low pH range we consider that the cation exchange resin and protonated PEI partially form polysalts, since the latter is formed when a polycation and a polyanion are mixed in the solution [20]. However, a 1:1 polysalt cannot be formed in this case because PEI is branched.

3.3. Adsorption behaviour

Fig. 4 shows the relationship between the adsorbed amount of PEI onto the cation exchange resin of Na^+ form and the immersion period. The amount is represented by the mole number of the nitrogen groups (amine and/or ammonium) adsorbed on the resin.

The amount of the adsorbed PEI increased rapidly in the beginning and then it reached an equilibrium. The higher the concentration of PEI the longer the period to reach the equilibrium.

In the literature there are different empirical expressions to define the isotherm equation [21]. The representation of the adsorption isotherm can be based on models with many parameters and

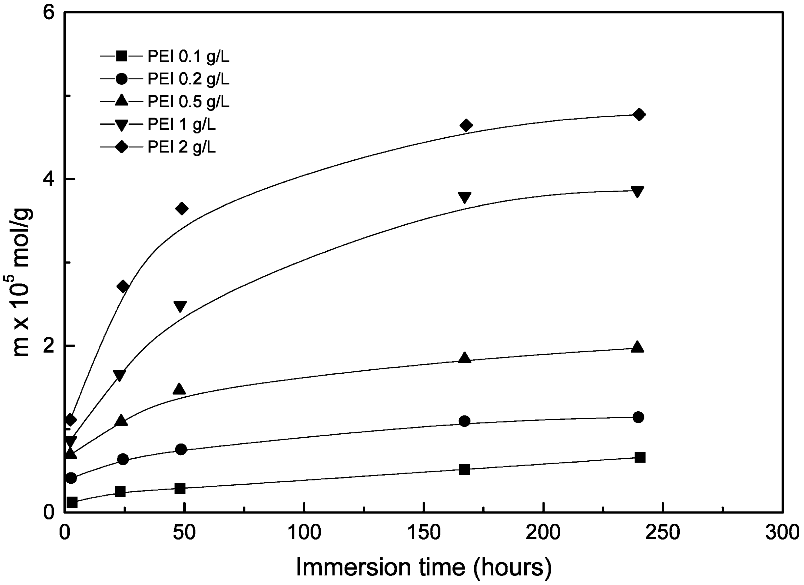

Fig. 4. Adsorption isotherms of PEI on the cation exchange resin as a function of immersion period for different initial concentrations.

among them are the Freundlich isotherm and Langmuir isotherm.

From different contact times between solid (bead) and solution of PEI, the plot of adsorbed amount of PEI versus concentration (values taken when the plateau was reached from $m = f$ (time) curves) represented in Fig. 5 indicated that Langmuir isotherm fitted well with experimental data.

Table 1 gives the constants A and B and the correlation coefficient R^2 corresponding to the two isotherm models used in this study. The good fitting of Langmuir isotherm can be seen. Moreover, the concentration m cannot increase indefinitely because a resin has a saturation level which was taken into account in the cited isotherm.

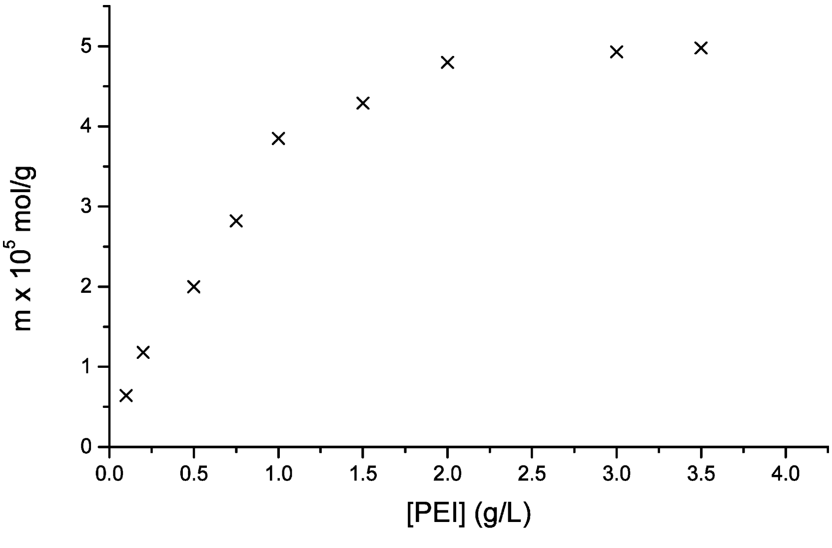

Fig. 5. Isotherm data for different initial concentration of PEI and exponential fit.

Table 1
Fitting result of the Langmuir and Freundlich isotherms

	$m = AC^{1/B}$ (Freundlich equation)	$m = AC/(1+BC)$ (Langmuir equation)
A	2.988	7.3346
B	1.696	1.1401
R^2	0.8616	0.9513

The best fit by Langmuir isotherm was given by Eq. (2)

$$m\ (10^{-5}\ \mathrm{mol\ g^{-1}}) = \frac{7.3346C}{1 + 1.14C} \qquad (2)$$

It was also found that experimental data fit quite well with value given by this equation.

Another equation has been found and fit well again with experimental data. This equation was the exponential function performed by the software (Origin 5.0) resulting from first-order experimental decay fitness.

The function is given by Eq. (3)

$$m\ (10^{-5}\ \mathrm{mol\ g^{-1}}) = 5.15 - 5.13\ \mathrm{e}^{C/0.859} \qquad (3)$$

3.4. Influence of pH

In the literature [22], previous works suggested that the point of zero charge on the PEI molecule is approximately at pH 10.8. This value was supported by mobility data showing that the effective charge to size ratio increased greatly between pH values 11 and 8 (note that pK_a value was found to be 8.8) but only slightly with further pH lowering down to 4. At pH 8.8, 50% of amino groups were protonated, at pH 9.0, 32% were protonated, while at pH 4 twice that amount of 64% of the amino groups were protonated. Hydration increased with decreasing pH. The small increase in mobility was caused by increased hydration and expansion of molecule from pH 9 to 4.

Fig. 6 shows the fixation isotherms of copper ions at different pH values of initial PEI aqueous solution.

It can be seen from Fig. 6 that the capacity–time curve became more flat in all cases as the pH value was decreased to a very low value or increased to a very high value. It also appeared that the amount retained decreased by lowering the pH for a fixed time (except at pH 9.76). This is a direct consequence of the excess migration of PEI when the

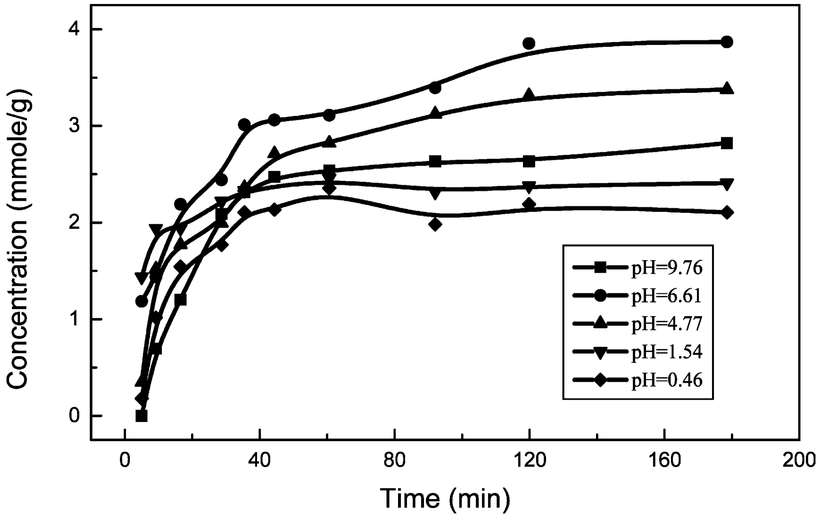

Fig. 6. Fixation curves of copper ions on the modified cation exchange resin; modification at 20 °C, PEI 1 g l^{-1} and immersion 1 week.

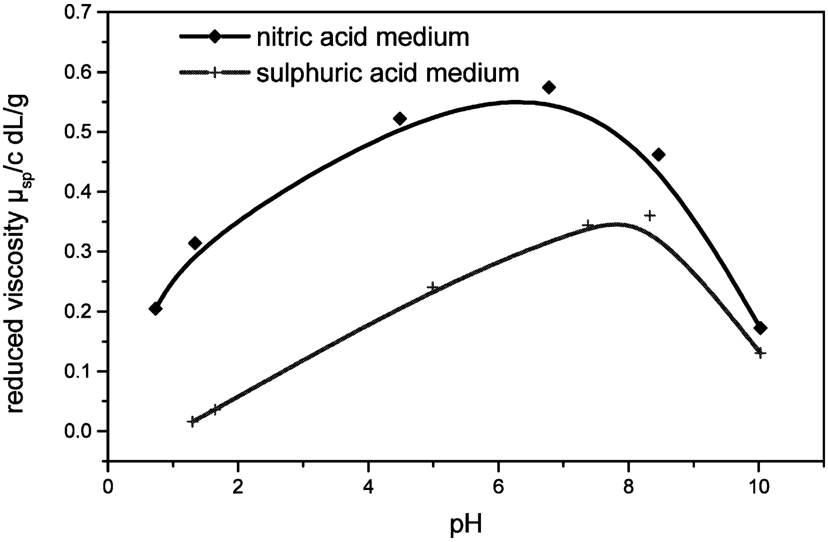

Fig. 7. Reduced viscosity of PEI 1 g dl^{-1} versus pH in nitric acid and sulphuric acid medium.

protonation degree was not very high or not very low. Indeed, the maximum of fixed copper concentration on modified resin reached the highest value 4 mmol g^{-1} at pH 6.61 followed by the pH 4.77.

The fixed copper concentration obtained at very acidic medium, pH 0.46, was smaller than that of unmodified resin. This fact can explain the absence of the complex Cu^{2+}–PEI formation or the low adsorption of PEI onto the resin at this pH.

At very low pH, PEI was highly protonated (depending on the nature of the counterion [23] the maximum protonation degree was about 70%) and at very high pH, the protonation degree stretched to zero. The behaviour of PEI on the cation exchange resin seemed to be almost the same as in solution. Reduced viscosity measured for protonated PEI in aqueous solution as a function of pH in the case of nitric acid and sulphuric acid are shown in Fig. 7. The reduced viscosity of PEI increased gradually with pH or protonation ratio, as the polyelectrolyte was protonated with either sulphuric acid or nitric acid until reaching a maximum at pH ~ 7. It appeared that the electrostatic repulsion was the predominant factor, which determined the viscosity tendency of all protonated PEI in those media. When the pH increased, the protonation ratio decreased and the opposite trend in viscosity was observed.

A similar behaviour was observed in both acidic media. However, the values of the reduced viscosity in the case of nitrate medium were higher. This can further be explained by the difference of association between ammonium groups and single- or double-charged anion.

4. Application to separation of metallic ions

In Table 2 are given the relationships between modification of cation exchange resin and water content, and Table 3 summarizes the selectivity

Table 2
Water content of the modified cation exchange resin

Resin	Water content (%)
Resin 0	56.8
Resin 1	57.1
Resin 2	64.3
Resin 3	51.4
Resin 4	62.5

Resin 0: unmodified resin; resin 1: modified resin in PEI 0.1 g l^{-1}, immersion period 1 week, pH 6.24 (controlled by HNO_3); resin 2: modified resin in PEI 1 g l^{-1}, immersion period 1 week, pH 6.61 (controlled by HNO_3); resin 3: modified resin in PEI 1 g l^{-1}, immersion period 1 week, pH 9.76 (controlled by HNO_3) and resin 4: modified resin in PEI 1 g l^{-1}, immersion period 1 week, pH 5.95 (controlled by H_2SO_4).

Table 3
Separation of metal couples

$M1/M2=S^{M_1}_{M_2}$	Ag–K	Ag–Li	Ag–Cu	Ag–Cd	Ag–Fe	K–Li	Cu–K	K–Cd	K–Fe	Cu–Li	Cd–Li	Fe–Li	Cu–Cd	Cu–Fe	Cd–Fe
Resin 0	2.06	3.01	1.27	1.69	2.84	1.43	1.36	1.22	1.49	2.43	1.79	1.24	1.33	1.96	1.63
Resin 1	2.00	3.15	1.13	1.44	2.74	1.02	2.75	1.15	1.30	3.88	2.04	1.33	2.42	3.60	1.12
Resin 2	2.11	3.86	0.21	2.65	2.23	1.28	5.68	1.82	1.35	8.39	2.34	1.73	5.02	5.20	1.34

factor of both modified and unmodified cation exchange resins for different pair of ions. As described in Section 2, batch sorption procedures were carried out by mixing weighed amounts of dry resin with the aqueous metal solution for 2 h with stirring until the equilibrium was reached. The remaining metal in the solution was determined by AAS and the amount of metal loaded on the resin phase was calculated by applying the mass balance.

Water content increased with decreasing pH and slightly decreased in the case of resin modified with PEI protonated by sulphuric acid. Except for resin 3, the hydration increased after modification in most cases, indicating hydrophilic properties of resulting resin.

Remarkable separation between copper and other ions was observed. Selectivity coefficient obtained for the separation between copper and alkaline ions attained the values 8.39 and 5.68 in the case of Li^+ and K^+, respectively. The higher the initial concentration of PEI the better the separation between heavy metals and alkaline ions. This modified resin was recently applied to purify the industrial wastes by column sorption and its performance was compared with the classical treatment and electrodialysis [24]. Good separation could be obtained using successively three kinds of resins (modified by PEI, tetrabutylammonium and unmodified resin) in the same set-up.

5. Conclusion

This study showed that a modification of the cation exchange resin surface by impregnation in PEI solutions allowed a selectivity improvement. The cation exchange resin became more selective towards the transition elements. The selectivity towards alkaline ions decreased because repulsion effects within cationic layer increases.

According to the result obtained for the pH influence, it appeared that the immersion of the resin in protonated PEI was better when the medium permitted a partial protonation of PEI and consequently the amount of PEI adsorbed decreased simultaneously in acidic medium or at pH of zero charge of polymer.

The capacity for copper fixation increased by raising the amount of PEI adsorbed. The exchange of alkaline ions was not affected when the initial PEI concentration was inferior to 1 g l^{-1} and then decreased with increasing of PEI adsorption.

Langmuir isotherm fitted well with experimental data and the exponential equation was found to be more adapted to describe the adsorption evolution.

Finally, it can be concluded that a synergic effect was observed in the case of the modified resin, i.e. copper ions retention occurred by both exchange and complexation mechanisms.

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