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Sezin Islamoglu Kadioglu[a]; Levent Yilmaz[a]; H. Onder Ozbelge[a]
[a] Middle East Technical University, Department of Chemical Engineering, Ankara, Turkey

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Estimation of Binding Constants of Cd(II), Ni(II) and Zn(II) with Polyethyleneimine (PEI) by Polymer Enhanced Ultrafiltration (PEUF) Technique

Sezin Islamoglu Kadioglu, Levent Yilmaz, and H. Onder Ozbelge
Middle East Technical University, Department of Chemical Engineering,
Ankara, Turkey

Abstract: Continuous and batch processes of polymer enhanced ultrafiltration for the estimation of binding constants of divalent cadmium, nickel, and zinc ions have been elaborated. Polyethyleneimine was used as a complexation agent. Effect of pH and ionic strength on the binding ability of target metal ions to polyethyleneimine were estimated by continuous mode PEUF system. A mathematical model was developed to estimate apparent complexation constants of metal ions with PEI. The development of this model, which is in good agreement with experimental data, enables to compare the data obtained in both continuous and batch system and correlate the effect of pH and ionic strength with apparent binding constants.

Keywords: binding constant, heavy metals, ionic strength, polyethyleneimine, ultrafiltration

INTRODUCTION

Interactions between macromolecules and different metal ions are an interesting field of study due to potential analytical and technological applications (1–3). One of the important technological applications of that field is heavy metal removal by ultrafiltration (UF) technique.

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Address correspondence to Sezin Islamoglu Kadioglu, University of Oklahoma, Department of Civil Engineering and Environmental Science, Norman, OK, 73019 USA.

The idea of adding a synthetic soluble macrocomplexation agent for industrial separation was first proposed by Michaels in 1968 (4). This idea constitutes the basis of complexation enhanced ultrafiltration (CEUF) in which metallic species bound to macromolecular complexing agent can be retained by the membrane while water and non-complexed ions pass through the membrane. CEUF can be classified according to the complexation agent used; micellar enhanced ultrafiltration (MEUF), colloidal enhanced ultrafiltration (CoEUF), and polymer enhanced ultrafiltration (PEUF).

In PEUF, water-soluble polymers are used as a complexation agent to bind metals to form macromolecular complexes, the membrane is just a barrier that has to retain everything bound to the polymer and allow permeation of all unbound components (5). Thus, selective and efficient separation of ions can be achieved.

Water-soluble synthetic polymers used in PEUF processes may be non-ionic, or they may be polyelectrolytes, possessing many ionizable groups that give rise to anionic or cationic character in aqueous solution or they may be polychelatogens (6,7), bearing functional groups with the ability to form coordination bonds.

Among the water soluble polymers, polychelatogens are preferable polymeric ligands in heavy metal removal from aqueous solutions, because of their affinity towards transition metals and inactivity towards alkali and alkali earth metals (5). One of the well known example of this group is poly(ethylenimine) (PEI), which has high binding ability, because of having unshared electron pair on the nitrogen atom which can form donor bonds with coordination unsaturated transition metals (8). Under normal conditions for synthesis, the polymer has a high degree of branching at the amine nitrogens (9). A typical PEI of MW 60000 contains ca. 350 primary amines, ca. 700 secondary amines, and ca. 350 tertiary amines (10) and it has chelating sites both in the main chain and side chains. In the previous studies, PEI was used for copper, nickel, lead, chromium, mercury, and arsenic removal from multi-component solutions of different origins (11–13), removal of components from natural waters, groundwater, (14) and seawater (15).

For the processes dealing with interactions between polymers and different metal ions, knowing the binding (complexation) constants of various metal-polymer complexes and the corresponding average coordination number for such polymeric solutions is important. They were usually determined either from potentiometric or pH titration curves by Bjerrum's method (16–18), or by a spectroscopic method through the molar absorption coefficient of the bound metals and the peak position in the spectra (19,20), or by the equilibrium dialysis method using an ion exchange membrane (21). Recently ultrafiltration is used as a preferable alternative method to estimate the binding constants of metals with various polyelectrolytes and polychelatogens.

The first attempt for theoretical modeling for the determination of the equilibrium constant for the formation of a complex between a metal ion and water soluble macroligand by batch ultrafiltration technique was made by Nguyen et al. (22). The case of one metal reacting with a polyacidic chelating agent was considered with the following assumptions:

The ligand groups on the polymer chain behave as independent complexing groups;

- Only 1:1 complexes form.
- The metal-polymeric complex is completely retained by the membrane.
- There is no interaction between the membrane and free metal ions.
- Protonated form of the ligand is not capable of forming complexes with the metal ions, complexation occurs only between the metal ions and non-protonated form of the ligand.

This proposed model in Nguyen's study (22) can be applied for the estimation of binding constants of metals with polyacids or polymeric agents that have acidity constants easily determined by potentiometric titration methods. However, as far as polyethyleneimine is concerned, the presence of three different amine functional groups (primary, secondary, and tertiary) complicates the calculation of the protonation constants of this polymer (23) and inaccurate results may be obtained because of the errors coming from the determination of protonation constants of PEI.

Buffle and Staub (24) developed a theoretical relationship which permit the computation of concentrations and equilibrium constants and test them with known ligands. Important features of that study are; other than 1:1 complexes between Zn-calgamite and Zn-tiron, 1:n complexes of Zn in natural medium were also studied.

In another study, using poly acrylic acid (PAA) used as a complexing agent and the equilibrium binding constants of Cu^{2+}, Ag^{+}, Ni^{2+}, Cd^{2+} were investigated taking into account the 1:n binding of metal ions to macroligand (25).

Effect of metal hydrolysis on the investigation of the equilibrium constants was first analyzed by Juang (26) and Volchek (27). This model was for polymer binding/ultrafiltration process for a multicomponent solution containing the ions of several metals, each of which is capable of forming coordination complexes with a polymeric complexing agent introduced into solution (27). Free ligand concentration in feed solution can be calculated by iterative procedure and based on this value rejection coefficient of each metal can be predicted if the protonation constant of the ligand is known. It was reported that, the computations given in that study are accurate if the volume of the feed solution remain more or less constant.

All the aforementioned models are derived by the equilibrium data obtained from batch ultrafiltration systems. In the systems that are operating in batch mode, permeate and retentate streams are not recycled back to the feed tank, this produces a substantial change in the composition of the feed solution, leading to a shift in the chemical equilibrium, which causes a change in the degree of metal binding and retention values. If the retention value of the metals can be kept constant throughout the process, theoretical models based on the experimental parameters (i.e., retention, metal/polymer ratio) can be improved in terms of their accuracy. This may be achieved by the application of semi-continuous and/or continuous mode of ultrafiltration processes.

Equilibrium studies in semi-continuous mode ultrafiltration systems were made by Canizares et al. (28). A mathematical model used in this study was based on the model previously derived by Volchek (27). The model was derived from conservation equations and analyses of equilibrium reactions in an aqueous solution.

In this study, we have tried to obtain a better understanding of the retention mechanism using a simple equilibrium model. Rather than trying to develop a universal model suitable for any metal and polymer system, an attempt has been made to adopt previous models used to estimate polymer-metal binding constants by batch PEUF method to continuous mode PEUF system. If the proposed model can be applicable for both batch and continuous mode PEUF systems and can give comparable results (i.e., similar apparent binding constants), then the results of the batch mode experiments can be used to predict the performance of a continuous mode PEUF system. This gives rise to the scaling-up for industrial processes, since these systems can handle larger effluent volumes and various types of commercial membranes with different configurations.

Bearing in mind the benefits of continuous mode PEUF operation, developing an equilibrium model which allows:

- To determine the relation between the retention values of the metal ions to the complexation constants involved in the polymer-metal complexation reaction in continuous mode PEUF operation
- To compare the equilibrium data obtained from the batch mode and continuous mode ultrafiltration systems will be important outcomes of this study.

THEORY

Binding constants of Cd^{2+}, Ni^{2+}, Zn^{2+} with polyethyleneimine (PEI) were calculated according to the model which is based on the following assumptions:

- There is no interaction between free metal ions with the membrane, that is free metal ions are not retained by the membrane.
- Retention of unbound PEI, is the same as that of the metal-PEI complex.
- Formation of insoluble metal hydroxy complexes were assumed to be negligible since the formation of insoluble metal hydroxy complexes is not favorable in the pH range studied (pH 5–6.5).
- Concentration polarization and/or membrane fouling does not occur in the concentration range studied.
- Only the non-protonated form of the PEI has the ability to form complexes with metal ions whereas the protonated form of the ligand (PEI) is inactive towards the metal ions.

For a single or multi-component solution containing the ions of several metals, each of which is capable of forming coordination complexes with PEI, following reactions were assumed to be occurring in the solution:

The formation of metal-PEI complexes:

$$M + nPEI \rightleftarrows M \cdot PEI_n$$

Protonation of PEI molecules depending on the acidity level of the solution:

$$H + PEI \rightleftarrows PEI \cdot H$$

The ionic charges have been omitted because they are not significant for modeling the process.

For a solution containing a total metallic species concentration $[\mathrm{M}]_\mathrm{t}$ and a total water-soluble polymeric agent $[\mathrm{PEI}]_\mathrm{t}$, loading is defined as:

$$\mathrm{L} = \frac{[\mathrm{M}]_\mathrm{t}}{[\mathrm{PEI}]_\mathrm{t}} \tag{1}$$

In contrast to the metal-ligand complex, free metal ions can pass through the membrane. The free metal concentration in the permeate may be expressed as $[M]_p$ and the retention coefficient is defined as:

$$R = 1 - \frac{[M]_p}{[M]_t} \tag{2}$$

And the apparent binding constant K_{app} of complexes by:

$$K_{app} = \frac{[M \cdot PEI_n]}{[M][PEI]^n} \tag{3}$$

Where

$[M{\cdot}PEI_n]$: total concentration of complexed metallic species
$[M]$: total concentration of non complexed metallic species
$[PEI]$: total concentration of free water soluble polymer
n: the number of ligand molecules per metal ligand complex

The total concentrations of metallic and ligand species are given by relations:

$$[M]_t = [M]_p - [M \cdot PEI_n] = [M] - [M \cdot PEI_n] \tag{4}$$

$$[PEI]_t = [PEI] + n[M \cdot PEI_n] \tag{5}$$

By substituting the equations 1, 3, 4, and 5 into the relation (2) we obtain:

$$[K]_{app} = \frac{R}{(1-R)[PEI]_t^n[1-nLR]^n} \tag{6}$$

Apparent binding constants of Cd^{2+}, Ni^{2+}, and Zn^{2+} with PEI were determined from measurements of R, L, and $[PEI]_t$. Loading (L) and $[PEI]_t$ are predetermined quantities and retention values were obtained experimentally. The only quantity that can not be determined experimentally is the number of ligand molecules per metal ligand complex. The number of PEI ligands participating in the complex formation with divalent metal ions was found to be either one, two, or more than two amino groups, depending on the conditions (29).

The presence of three different amine functional groups (primary, secondary, and tertiary) in diverse proportions complicates the estimation of the number of PEI ligands (n) participating in the complex formation with divalent metal ions. Different speculations have been made based on the results of UV-visible spectroscopic titration analysis of the complexes. In one of the previous studies, stoichiometry of complex 1:1 (ML) was assumed and n is taken as 1 for Ni-PEI complex and polymer repeat unit comprising seven monomer units (C_2H_5N) was considered to be the ligand at pH 5 (23). In cases where a single monomer unit is considered as a ligand, n (the number of PEI ligands participating in the complex formation with divalent metal ions was taken as 2.1 and 2.3 at pH 6 and pH 5 respectively.

In this study, each monomer unit is considered as ligand and complex formation is simply considered to proceed in a single step as it was assumed in several previous papers (30,31). For the number of ligand molecules per metal ligand complex only $n = 2$ is taken into account for the target metals. Although pH does not appear in the equations of the proposed model, for the three target metals (Cd^{2+}, Ni^{2+}, Zn^{2+}), the effects of pH and ionic strength on the degree of binding were considered. For this reason, the complexation constant was named apparent binding constant. Impacts of low pH values and high salt concentrations were observed by estimating the apparent binding constants at different pH and ionic strength values.

EXPERIMENTAL

Materials

In the ultrafiltration experiments and in atomic absorption spectrometry analysis, polyethyleneimine (PEI) (Sigma) with average molecular weight of 60,000 Da, cadmium nitrate tetrahydrate $Cd(NO_3)_2 \cdot 4H_2O$ (Merck), zinc nitrate hexahydrate $N_2O_6Zn \cdot 6H_2O$ (Acros), nickelous nitrate hexa-hydrate $Ni(NO_3)_2 \cdot 6H_2O$ (J.T. Baker), sodium nitrate $NaNO_3$ (Merck), sodium sulfate anhydrous Na_2SO_4 (J.T. Baker), sodium hydroxide NaOH (Merck), nitric acid HNO_3 (Merck), and ultrapure water having a specific conductance of $18.3\,M\Omega\,cm^{-1}$ obtained from water purification system (Human Reverse Osmosis (RO)-UltraPure (UP) water purification systems) were used. All the chemicals used in this study were analytical grade reagents.

Apparatus

Continuous Mode System

For continuous mode ultrafiltration experiments SP20 ultrafiltration system was used. The system can accommodate spiral wound regenerated cellulose cartridges having an effective area of $0.93\,m^2$, and contains an integral reservoir which allows processing of feed volumes from 20 liters down to 1 liter. The flow is provided by a sanitary positive displacement lobe pump. The system is controlled by a dedicated microprocessor, which adjusts the pump speed and back pressure valve to enable optimal running conditions to be maintained throughout the process.

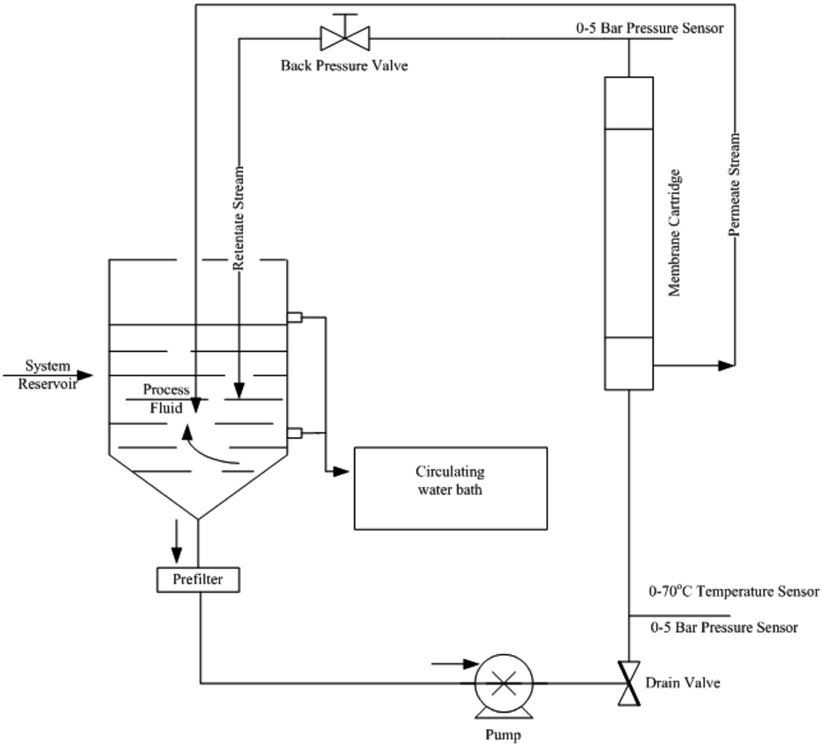

Figure 1. SP20 Pilot Scale ultrafiltration system (continuous mode).

Pressure of the feed side was 13 kPa and that of permeate side was 5 kPa, which produces a pressure gradient of 6 kPa. Each experimental run for PEUF process perpetuates for 3.5 hours to reach steady state. For particular application requirements several processing modes can be used. In this study a semi-automatic continuous processing mode is used (Fig. 1). In continuous processing mode both permeate and retentate streams are circulated back to the reservoir in order to keep the feed concentration constant. A circulating water bath was used in order to keep the temperature constant while the pH of the feed solution is monitored by a pH meter (WTW, Germany) throughout the experiment.

Batch Mode System

Batch mode ultrafiltration experiments were carried out on a lab-scale Model 8400 dead-end stirred membrane cell manufactured by Amicon-Millipore. The equipment has a cell capacity of 400 ml and its effective membrane area is 41.8 cm^2. The cell is placed on a magnetic stirrer to agitate the fluid inside the cell. Nitrogen gas cylinder is connected to the cell in order to pressurize the system. Pressure should not exceed 75 psi (0.01 Pa).

Membrane Cleaning

Membranes were cleaned before and after each experimental run by applying in place a cleaning procedure, i.e., they were kept in the module while the cleaning solutions were pumped through the system for a given period while the permeate and retentate streams were discarded. Prior to ultrafiltration experiments membrane cleaning was performed by osmosized water. Upon the completion of each experimental run, first, the system was stopped, drained, and flushed with osmosized water. Second, 0.1 M NaOH solution was flushed through the system for 15 min. During the cleaning procedure, transmembrane pressure was adjusted to the same value as in the experimental run, and the temperature was adjusted to 45°C. Third the system was drained and flushed with osmosized water. After that, 3 ml/l HNO_3 60% (v/v) solution was pumped through the system for 15 min. Finally, the system was drained again and flushed with osmosized water, until the pH of the permeate stream appeared to be in neutral pH range.

Philips PU9200X atomic absorption spectrophotometry (AAS) was used for the detection of metal in permeate samples.

RESULTS AND DISCUSSIONS

Retention behaviors of target metals at different pH and ionic strength were first tested by continuous mode ultrafiltration equipment. Then, with the predetermined pH values and salt concentrations, apparent binding constants of target metals with PEI were estimated by the proposed model. The results obtained from both continuous and batch mode operations were compared.

Effects of pH and Loading on Retention

Complexation tests for metals were made with 15 ppm metal solutions and varying polymer concentrations in the range where metal/polymer ratio remains between 0.05 and 1. Since the previous study (32) showed that retention is dependent on metal/polymer ratio rather than their individual concentrations, throughout the experiments, metal concentration was kept constant at 15 ppm and only relative amounts of metal and polymer were changed.

For the loading values lower than 0.01 (100:1 polymer:metal concentration ratio) decrease in retention was observed probably because of the decrease in the solubility of PEI and hence inefficiency in complex formation. To ensure favorable conditions for the process in further parts of the research, a maximum of 10-fold weight excess of the polymer with respect to the amount of metal present in the feed was used.

Although a complexation period of 2 hours is found to be sufficient to achieve complexation equilibria (33), PEI-metal mixtures were left for complexation for 12 hours throughout this study.

In Fig. 2, retention of cadmium ions at different acidity levels and metal/polymer ratios are shown. As seen from the figure, the pH has very profound effect on Cd^{2+}-PEI complexation and as a consequence on the amount of Cd^{2+} retained by the membrane. The extent of binding of Cd^{2+} by PEI at pH 6.5 and pH 6 was considerably superior to that at pH 5. At low loadings, retention values were almost the same and almost equal to 1 at pH 6.5 and pH 6 which means almost complete retention of cadmium ions can be achieved when the amount of polymer is at least 10-fold higher than the amount of metal in solution. As the metal/polymer ratio increases, the effect of the pH can be seen more

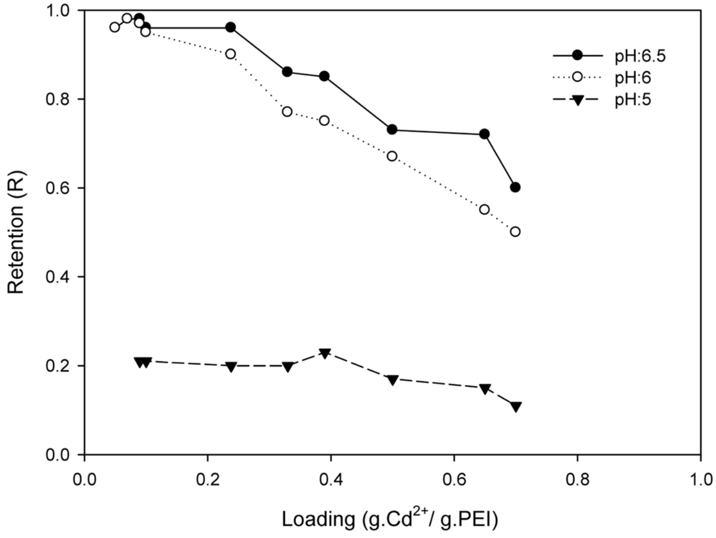

Figure 2. Effect of pH and loading on the retention profile of Cd^{2+}.

clearly since the retention values at pH 6 becomes lower than the retention values obtained at pH 6.5. This result is consistent with the results of previous studies in which it was reported that cadmium is highly responsive to pH alternation, and the complexation reaction between cadmium and PEI is favorable at pH 6.5 (34).

When pH was reduced down to 5, the process enabled a maximum retention of only 35%. Depending on loading values, 50–70% reduction in the amount of metal rejection was recorded as a consequence of pH reduction from 6.5 to 5. Such a strong dependence of the retention values on the acidity level of the solution may result from the changes in the binding ability of PEI at different pHs.

At higher pHs, amine groups are more available and can coordinate more easily with the metal ions. It was determined that only 0.00001% of the amine groups were deprotonated at pH 3, whereas at pH 5, the value reached 0.001%, and at pH 7, it was 0.1% (35). This means that there is a strong competition between the metal ions and protons for the electron pairs in the amine groups of PEI. This competition is favored for the metal ions at higher pH values; therefore effective binding of metal ions to the active sites of PEI molecules takes place at high pH levels.

As far as pH effect is concerned, same trend as in the case of Cd^{2+}-PEI binding was also observed for Ni^{2+} (Fig. 3). Binding of Ni^{2+} with PEI is favorable at pH 6.5 and pH 6 and the extent of complexation is decreased markedly when the pH of the solution is reduced down to 5.

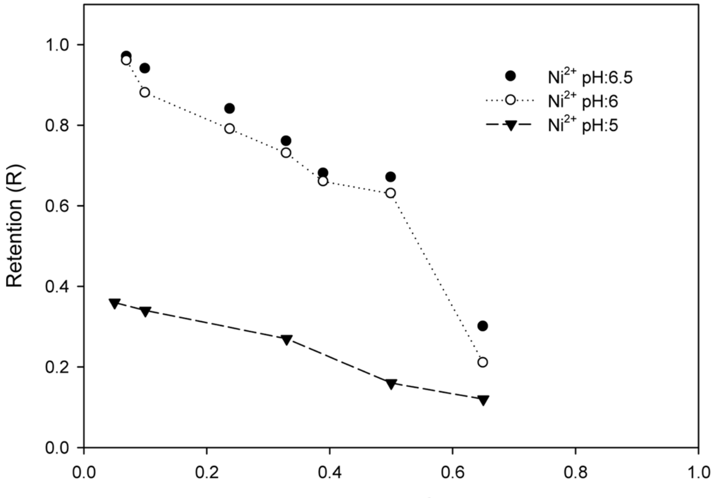

Figure 3. Effect of pH and loading on the retention profile of Ni^{2+}.

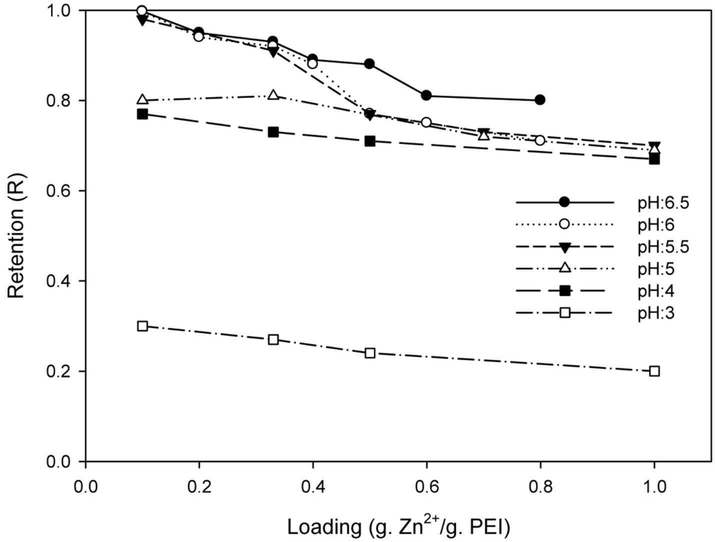

Figure 4. Effect of pH and loading on the retention profile of Zn^{2+}.

Depending on the amount of polymer in the solution 40–98% and 35–96% of Ni^{2+} can be retained by the membrane at pH 6.5 and pH 6 respectively. But when the pH is reduced to 5, because of the inhibition of binding ability of PEI due to protonation of amine groups, Ni^{2+} retention is decreased and the maximum retention was recorded to be 34%.

The binding ability of Zn^{2+} with PEI was tested in the pH range of 3–6.5 (Fig. 4). It was observed that, almost complete retention can be achieved at high pH values. In addition, PEI molecules retained zinc ions effectively down to pH 4. Zn^{2+} retention slightly decreased between pH 6.5 and 4, then a steep decrease (50–70%) in retention was observed at pH 3 because the protonation of amine groups leads to the release of zinc ions.

The effect of pH on zinc rejection is analogous to that of Cd^{2+} and Ni^{2+}, at pH 6.5 and 6. At pH 5 and less than 5, retention profile of Zn^{2+} ion is distinguished from the that of Ni^{2+} and Cd^{2+} ions in such a way that, at pH 5 neither Ni^{2+} nor Cd^{2+} ions can be retained significantly whereas 80% of Zn^{2+} retention can be achieved.

Effects of Ionic Strength on Retention

The effect of ionic strength on Cd^{2+} retention was examined at pH 6.5 and pH 6 by adding increasing amount of $NaNO_3$ into the solution. As shown in Fig. 5, at pH 6.5, where the binding ability of cadmium ions

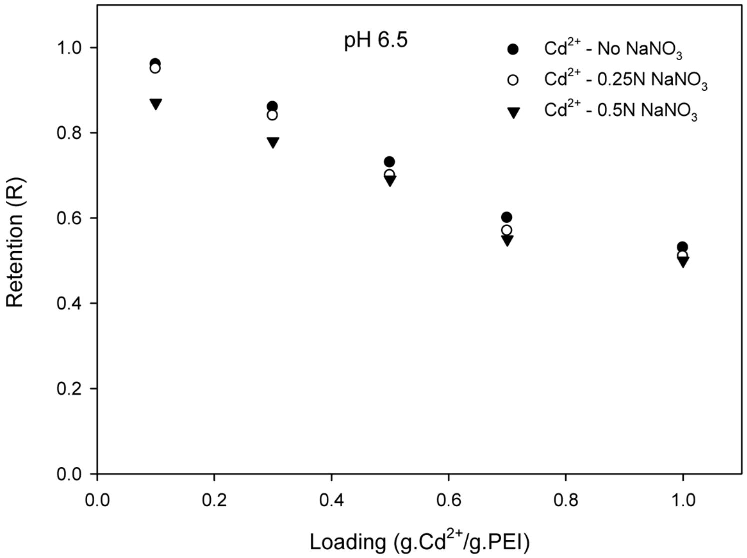

Figure 5. Effect of salt concentration on retention of Cd^{2+} at pH 6.5.

were proved to be maximum, the addition of 0.25 N $NaNO_3$ causes only 1–3% decrease in the retention values. By the further increase in salt concentration (0.5 N $NaNO_3$) retention drop was reported to be between 3–9%. Reduction in Cd^{2+} retention amounting to 1–9% is relatively insignificant.

At pH 6, the effect of salt addition was observed in a wider concentration range lying between 0.1 and 1 N $NaNO_3$ (Fig. 6). The effect of ionic strength on Cd^{2+} retention was observed to be more pronounced at pH 6 then pH 6.5 especially at high salt concentrations.

Decrease in the retention of Cd^{2+} started in the presence of 0.25 N $NaNO_3$, depending on the metal/polymer ratios 2–11% reduction in retention was recorded by the addition of 0.25 N $NaNO_3$. The extents of reduction in retention values were obtained to be in the range of 9–24% and 12–28% in the presence of 0.5 N $NaNO_3$ and 1 N $NaNO_3$, respectively.

Experiments for Ni^{2+} were performed in the presence of 0.5 N $NaNO_3$ at pH 6.5 (Fig. 7) and in the presence of 0.25 N and 0.5 N $NaNO_3$ at pH 6 (Fig. 8). An adverse effect of excess salt concentration on Ni^{2+} retention was observed to be more significant at pH 6 than pH 6.5.

This is parallel to the expectations, since Ni^{2+}-PEI complexation is favorable at pH 6.5, and the strength of the bond may probably be higher than the one formed at pH 6, therefore, it can withstand the changes in

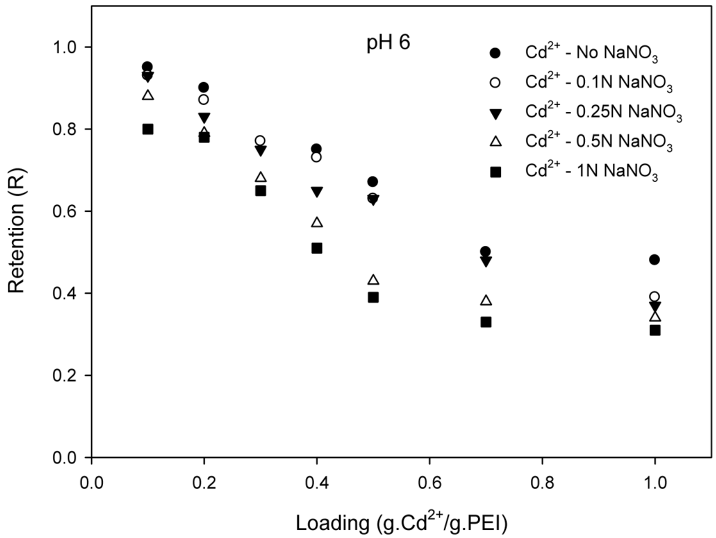

Figure 6. Effect of salt concentration on retention of Cd^{2+} at pH 6.

ionic strength. At pH 6, 1–8% and 9–28% reduction in retention values were recorded in the presence of 0.25 N and 0.5 N $NaNO_3$, respectively.

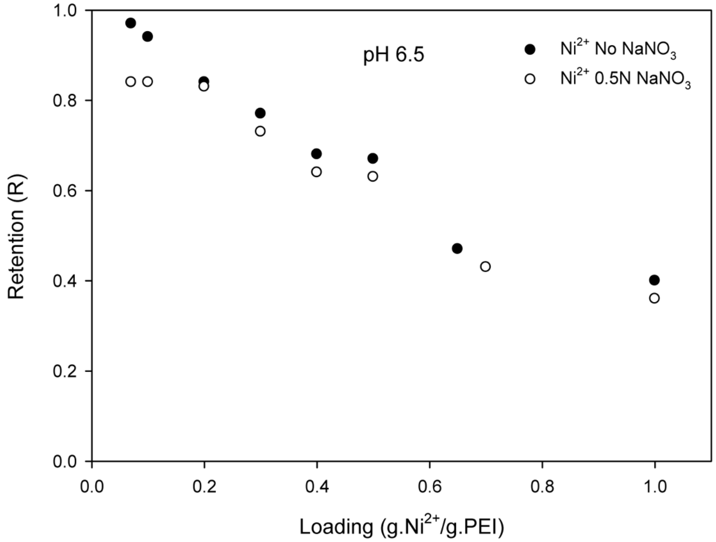

Figure 7. Effect of salt concentration on retention of Ni^{2+} at pH 6.5.

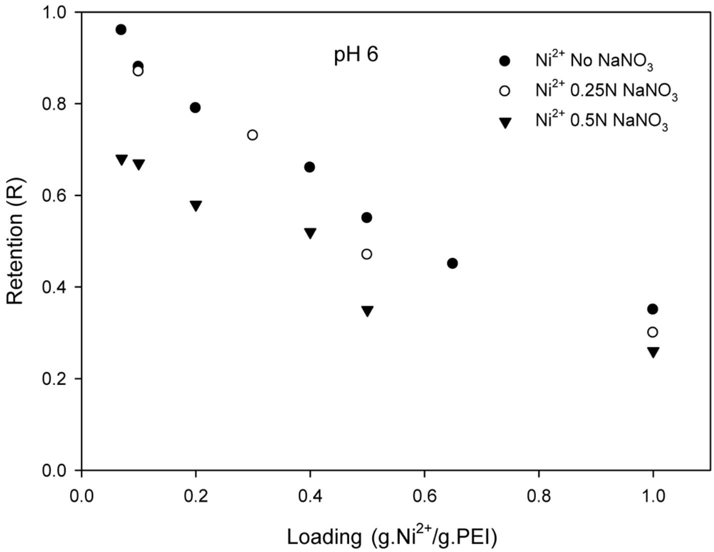

Figure 8. Effect of salt concentration on retention of Ni^{2+} at pH 6.

Among three target metals, the most drastic adverse effect of ionic strength was observed in the retention of Zn^{2+} especially at high loading values. In the presence of 0.5 N $NaNO_3$ and for the loading values greater than 0.5, approximately 45% and 55% decrement occurred in the retention of Zn^{2+} at pH 6.5 and pH 6, respectively (Figs. 9 and 10).

Estimation of K_{app}

Based on the Equation 6, the apparent binding constants of target metals with PEI were estimated. The apparent binding constants obtained in this study, together with those reported in the literature, are compiled in Table 1.

As is evident from Table 1, there is a good agreement between the apparent complexation constants estimated in this study and the ones cited in the literature, although parameters like pH, and the molecular weight of PEI may be different. For instance, PEI used in the study of Canizares et al. (23) has a molecular weight of 25000 Da and that of the one used in the potentiometric study was 30000 Da (36).

It is important to note that the metal-PEI complex formation constants estimated from the equations proposed in this study are conditional and affected by pH, actual metal concentration in aqueous

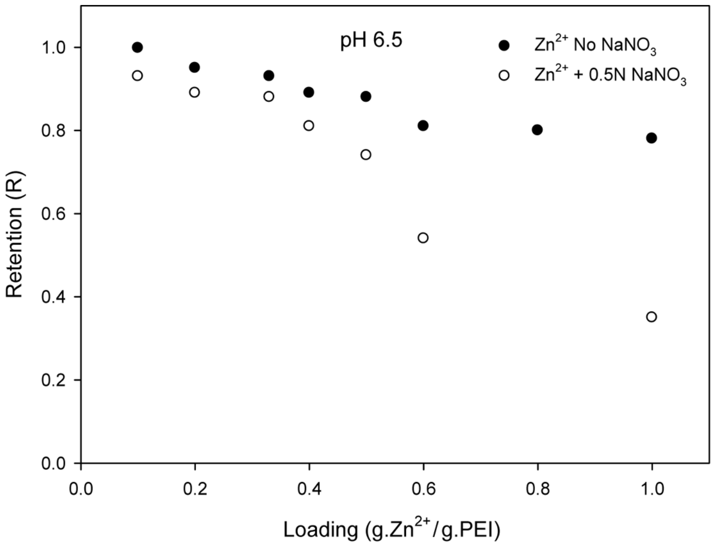

Figure 9. Effect of salt concentration on retention of Zn^{2+} at pH 6.5.

solutions, and salt concentration. These apparent complex formation constants are thus valid only for the conditions of the experiments. Generalization of such calculations on complexation by PEI in real waste

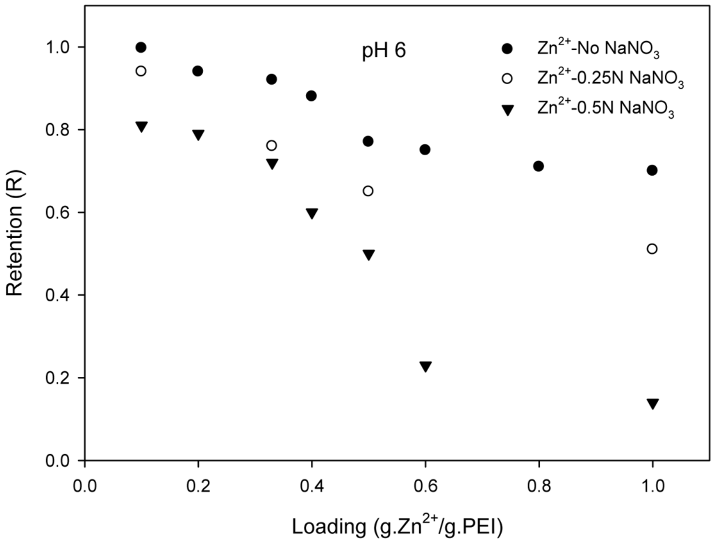

Figure 10. Effect of salt concentration on retention of Zn^{2+} at pH 6.

Table 1. Apparent complexation constants of metal ions with PEI

Metal	pH	N	logK (This Study)	logK (Ref.)	Method/Reference
Ni^{2+}	6	2	7.09	7.61	UV-Visible Spectrometry (23)
Cd^{2+}	6	2	7.27	7.84	Two phase potentiometry (29)
Zn^{2+}	6	2	10.41	11.1	Potentiometric titration (36)

waters would therefore require a large data set representing all the conditions of interest (pH, ionic strength, and ion composition) or a model that can account for such variations.

Effects of pH and Ionic Strength on K_{app}

Apparent binding constants of metal ions were calculated at predetermined values of $L = 0.1$, $[PEI] = 5 \times 10^{-3}$ M, $n = 2$ and at different pH values. The results were presented in Table 2. Although pH did not remain explicitly in governing equation (Eq. 6), different K_{app} values at different acidity levels exhibit the effect of pH on the degree of binding and as a consequence on the apparent binding constants.

As can be seen from Table 2, the apparent binding constant of Zn^{2+} was higher than that of Cd^{2+}, which in turn was higher than that of Ni^{2+}.

Table 2. Effect of pH on apparent complexation constants of metal ions

Metal	pH	$logK_{app}$
Cd^{2+}	6.5	6.17
	6	6.06
	5	4.06
Ni^{2+}	6.5	5.98
	6	5.64
	5	4.38
Zn^{2+}	6.5	7.49
	6	7.32
	5.5	6.48
	5	5.42
	4	5.27
	3	4.29

Table 3. Effect of salt concentration on apparent complexation constants of metal ions (calculations were made at predetermined values of L = 0.1, [PEI] = 5×10^{-3}, n = 2)

Metal	pH	$NaNO_3$ Concentration (N)	$\log K_{app}$
Cd^{2+}	6	0.1	5.9
	6.5	0.25	6.17
	6	0.25	5.9
	5	0.25	4.31
	6.5	0.5	5.59
	6	0.5	5.48
	6	1	5.30
Ni^{2+}	6	0.25	5.59
	6.5	0.5	5.48
	6	0.5	5.03
Zn^{2+}	6.5	0.5	5.90
	6	0.5	5.39
	6	0.25	5.98

In addition, the adverse effect of pH reduction can also be observed in apparent binding constants, which confirmed the results of PEUF experiments.

Same as pH, salt concentration did not remain explicitly in the governing equation of binding constants (Eqn. 6), but the adverse effect of ionic strength on the binding ability of cadmium, nickel, and zinc ions and hence on the binding constants can be observed from the data presented in Table 3.

Effect of Mode of PEUF Operation on the Estimation of K_{app}

In batch mode PEUF operation, the binding properties were documented in retention profiles, which are plots of the retention (R) versus the filtration factor (Z) (35). Z is defined as the ratio of the volume of the filtrate and the volume of the cell solution.

In order to build-up a connection between the batch and continuous mode studies, first of all, for the selected loading and pH values, retention values of cadmium, nickel, and zinc ions were determined by the PEUF experiments performed in batch mode by the dead end stirred membrane cell. As it was mentioned earlier, metal/polymer ratio does not remain constant throughout the batch processes because the permeate stream was continuously withdrawn from the membrane cell and causing a decrease in metal concentration and relative increase in polymer concentration in feed solution. In order to calculate the instant loading value in the membrane cell, several models have been developed. But, for the sake of simplicity, it was assumed that changes in the relative amounts of metal and polymer concentrations did not affect the loading value in batch mode experiments performed in this study. Since the experiments were performed for dilute metal mixtures containing a low amount of polymer, the assumption of the ineffectiveness of changes in metal concentration on loading was considered to be reasonable.

By substituting the loading, total polymer concentration and retention values obtained in batch mode experiments into Equation 6, apparent complexation constants of cadmium, nickel, and zinc were calculated and compared with the ones obtained by continuous mode PEUF experiments (Table 4).

As can be seen from Table 4, almost the same apparent binding constants are obtained both in batch and continuous mode operations. Therefore, it can be concluded that for dilute metal solutions containing relatively low amounts of polymer, by looking at the apparent constants calculated for batch systems, we may have an idea about the performance of PEUF systems operating in continuous mode and with the same conditions as the batch system.

Table 4. Comparison of K_{app} values obtained in continuous and batch PEUF systems

pH	Metal	[PEI]	n	R	L	$\log K_{app}$
6	Cd^{2+}	5×10^{-3}	2	0.95 (continuous)	0.1	6.06
6	Cd^{2+}	5×10^{-3}	2	0.98 (batch)	0.1	6.48
5	Cd^{2+}	5×10^{-3}	2	0.21 (continuous)	0.1	4.06
5	Cd^{2+}	5×10^{-3}	2	0.32 (batch)	0.1	4.33
6	Ni^{2+}	5×10^{-3}	2	0.88 (continuous)	0.1	5.64
6	Ni^{2+}	5×10^{-3}	2	0.86 (batch)	0.1	5.55
5	Ni^{2+}	5×10^{-3}	2	0.34 (continuous)	0.1	4.38
5	Ni^{2+}	5×10^{-3}	2	0.41 (batch)	0.1	4.52
6	Zn^{2+}	5×10^{-3}	2	1.00 (continuous)	0.1	7.32
6	Zn^{2+}	5×10^{-3}	2	0.99 (batch)	0.1	6.79
5	Zn^{2+}	5×10^{-3}	2	0.83 (continuous)	0.1	5.42
5	Zn^{2+}	5×10^{-3}	2	0.90 (batch)	0.1	5.73

CONCLUSIONS

In this study, the effects of ionic strength, pH, and metal/polymer ratio on the performance of continuous mode PEUF process have been examined. A model for PEUF process was developed and by the proposed model, the apparent binding constants of metal-PEI complexation reactions were estimated.

The following conclusions were drawn in respect of the results obtained in this study:

1. PEI has high binding ability towards the divalent ions of Cd^{2+}, Ni^{2+}, and Zn^{2+} at pH 6.5 and pH 6. PEI molecules retained cadmium and nickel ions effectively down to pH 6 and zinc ions down to pH 4. That means, cadmium and nickel are more sensitive to the changes in the acidity level of the solution.
2. By the addition of $NaNO_3$, depending on the concentration of $NaNO_3$, the extent of complexation between PEI and metal ions decreases and as a consequence the retentions of metals tend to decrease. For Cd^{2+} and Ni^{2+}, at pH 6.5 and 6, the addition of low amounts of $NaNO_3$ did not change the degree of retention, and the adverse effect of salt addition can be observed upon the addition of high amounts of salt (i.e., $>0.5\,N\ NaNO_3$). Among the three metals, the most drastic adverse effect of ionic strength was seen on Zn^{2+} retention especially at high loading values.
3. Based on the proposed model, the binding constants were calculated and compared with the ones cited in the literature. Proximity of the apparent constants which were estimated in this study and the ones estimated by potentiometric and/or spectrometric methods, indicate that the continuous mode-PEUF method can be used to predict the apparent binding constants of metals with polymeric agents. For dilute metal solutions and in the presence of low PEI concentrations, approximately the same apparent binding constants were obtained based on the data obtained by batch and continuous mode PEUF operations. Therefore, it can be concluded that, by estimating the apparent constants calculated for batch systems, the idea about the performance of PEUF systems can be obtained as far as the same conditions have been established.

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REFERENCES

1. Islamoglu, S.; Yilmaz, L.; Ozbelge, H.O. (2006) Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents. *Sep. Sci. Technol.*, *41* (15): 3367.
2. Oktar, C.; Yilmaz, L.; Ozbelge, H.O. (2008) Selective mercury uptake by polymer supported hydroxyethyl sulfonamides. *React. Funct. Polym.*, *68* (4): 842.
3. Dilek, C.; Ozbelge, H.O.; Bicak, N. (2002) Removal of boron from aqueous solutions by continuous polymer-enhanced ultrafiltration with polyvinyl alcohol. *Sep. Sci. Technol.*, *37* (6): 1257.
4. Michaels, A.S. (1968) *Advances in Separation and Purification*; Chapter: Ultrafiltration, Perry, E.S. ed.; Wiley: New York, NY.
5. Geckeler, K.E.; Volchek, K. (1996) Removal of hazardous substances from water using ultrafiltration in conjuction with soluble polymers. *Environ. Sci. Technol.*, *30* (3): 725.
6. Islamoglu, S.; Yilmaz, L. (2006) Effect of ionic strength on the complexation of polyethyleneimine (PEI) with Cd^{2+} and Ni^{2+} in polymer enhanced ultrafiltration (PEUF). *Desal.*, *200* (1–3): 288.
7. Doganay, C.O.; Ozbelge, H.O.; Yilmaz, L.; Bicak, N. (2006) Removal and recovery of metal anions via functional polymer based PEUF. *Desal.*, *200* (1–3): 286.
8. Juang, R.S.; Chiou, C.H. (2000) Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers. *J. Membr. Sci.*, *177* (1–2): 207.
9. Johnson, T.W.; Klotz, M.I. (1974) Preparation and characterization of some derivatives of poly(ethlenimine). *Macromol.*, *7* (2): 149.
10. Suh, J.H. (1996) *Polymeric Materials Encyclopedia*; page 4210 and 8230. Salamone, K.C. ed.; CRC Press: Boca Raton.
11. Strathmann, H. (1980) Selective removal of heavy metal ions from aqueous solutions by diafiltration of macromolecular complexes. *Sep. Sci. Technol.*, *15* (4): 1135.
12. Legault, A.; Volchek, K.; Tremblay, A.; Whittaker, H. (1992) Removal of arsenic from groundwater using reagent binding/membrane separation. *AIChE Annual Meeting*; In Proceedings, November 1–6 1992, Miami, Florida.
13. Buckley, L.P.; Vijayan, S.; McConeghy, G.J., et al. (1990) Removal of soluble toxic metals from water. *Technical Report AECL10174, Report of the Atomic Energy of Canada Ltd.*, Chalk River.
14. Dytnersky, Y.; Hojainov, Y. (1991). Extraction and utilization of valuable components from ocean water. Desalination, *81*:1–3, 261–264.
15. Mandel, M.; Leyte, J.C. (1964) Interaction of polymethacrylic acid and bivalent counterions. *J. Polym. Sci., Part A*, *2*: 2883.
16. Gregor, H.P.; Luttinger, L.B.; Loebl, E.M. (1955) Metal polyelectrolyte complexes: The polyacrylic acid-copper complex. *J. Phys. Chem.*, *59* (1): 34.
17. McLaren, J.V.; Watts, J.D.; Gilbert, A. (1967) Interactions of nickel and copper with polyacrylic acid. *J. Polm. Sci. Part C.*, *16*: 1900.

18. Leyte, J.C.; Zuiderweg, L.H.; Reisen, M. (1968) A spectroscopic study of binuclear copper complexes in aqueous polymethacrylic acid solutions. *J. Phys. Chem.*, *72* (4): 1127.
19. Wall, F.T.; Gill, S.J. (1954) Interaction of cupric ions with polyacrylic acid. *J. Phys. Chem.*, *58* (12): 1128.
20. Yamaoka, K.; Masujima, T. (1979) Spectroscopic and equilibrium dialysis studies of the polyacrylic acid-copper complex in the pH range 3,5–7. *Bull. Chem. Soc. Jp.*, *52* (6): 1819.
21. Nguyen, Q.T.; Aptel, P.; Neel, J. (1980) Application of ultrafiltration to the concentration and separation of solutes of low-molecular weight. *J. Membr. Sci.*, *6* (1): 71.
22. Canizares, P.; Lucas, A.; Perez, A.; Camarillo, R. (2005) Effect of polymer nature and hydrodynamic conditions on a process of polymer enhanced ultrafiltration. *J. Membr. Sci.*, *253* (1–2): 149.
23. Buffle, J.; Staub, C. (1984) Measurement of complexation properties of metal ions in natural conditions by ultrafiltration: Measurement of equilibrium constants for complexation of zinc by synthetic and natural ligands. *Anal. Chem.*, *56* (14): 2837.
24. Rumeau, M.; Persin, F.; Sciers, V.; Persin, M.; Sarrazin, J. (1992) Separation by coupling ultrafiltration and complexation of metallic species with industrial water soluble polymers. Application for removal or concentration of metallic cations. *J. Membr. Sci.*, *73* (2–3): 313.
25. Juang, R.S.; Liang, J.F. (1993) Equilibrium studies for the interaction of aqueous metal ions and polyacrylic acid by a batch ultrafiltration method. *J. Membr. Sci.*, *82* (1–2): 163.
26. Volchek, K.; Krentsel, E.; Zhilin, Yu, Shtereva, G.; Dytnersky, Yu. (1993) Polymer binding/ultrafiltration as a method for concentration and separation of metals. *J. Membr. Sci.*, *79* (2–3): 253.
27. Canizares, P.; Perez, A.; Camarillo, R.; Linares, J.J. (2004) A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents. *J. Membr. Sci.*, *240* (1–2): 197.
28. Jarvis, N.V.; Wagener, J.M. (1995) Mechanistic studies of metal ion binding to water-soluble polymers using potentiometry. *Talanta*, *42* (2): 219.
29. Ouiminga, S.A.; Brandebourger, M.; Chaufer, A.; Deratani, A.; Sebille, B. (1987) Preparation of water soluble chelating aminated starch derivatives and their use for the concentration of metal ions by ultrafiltration. *React. Polym.*, *5* (2): 111.
30. Masse, P.; Choe, T.B.; Verdier, A. (1987) Separation of Cu-Ni by a complexation ultrafiltration method. *Annali Chimica.*, *77*: 925.
31. Uludag, Y.; Ozbelge, H.O.; Yilmaz, L. (1997) Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration. *J. Membr. Sci.*, *129* (1): 93.
32. Muslehiddinoglu, J.; Uludag, Y.; Ozbelge, H.O.; Yilmaz, L. (1998) Effect of operating parameters on selective separation of heavy metals from binary mixtures via PEUF. *J. Membr. Sci.*, *140* (2): 251.

33. Muslehiddinoglu, J.; Uludag, Y.; Ozbelge, H.O.; Yilmaz, L. (1998) Determination of heavy metal concentration in feed and permeate streams of polymer enhanced ultrafiltration process. *Talanta*, *46* (6): 1557.
34. Rivas, B.L.; Pooley, S.A. (2005) Water-soluble amine and imine polymers with the ability to bind metal ions in conjuction with membrane filtration. *J. App. Polym. Sci.*, *96* (1): 222.
35. Kobayashi, S.; Kazuhisa, H.; Masazumi, T.; Saegusai, T. (1987) Chelating properties of linear and branched Poly(ethylenimines). *Macromol.*, *20*: 1496.