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# Removal of Heavy Metals from Multicomponent Metal Mixtures by Polymer Enhanced Ultrafiltration: Effects of pH, Ionic Strength and Conformational Changes in Polymer Structure

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**Fractional separation of industrially important heavy metals (cadmium, nickel, zinc) from binary and ternary metal mixtures by continuous mode polymer enhanced ultrafiltration was studied. Polyethyleneimine (PEI) was used as a complexation polymer. Effects of pH and ionic strength on process efficiency were investigated. To gain insight about the characteristics of binding between highly branched PEI and metal ions and effect of salt concentration on this binding were investigated by performing dynamic and static light scattering measurements. It was observed that with optimum pH and salt concentration, fractional separation of metals can be achieved.**

**Keywords** heavy metal; light scattering; polyethyleneimine; polymer; ultra filtration; zinc

## INTRODUCTION

Wastewaters from industrial processes (i.e., hydrometallurgical, agricultural, coal, natural gas, paper, mining, electroplating, etc.) usually contain high concentrations of heavy metal ions such as $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$, Cr(VI), etc. (1). Selective separation of these metal ions from industrial and waste streams is crucial from both industrial and environmental viewpoints. Developments in separation processes are in the way of establishing cost-effective methods for fractional separation and recovery of heavy metals (2). Although much work has been devoted to this topic over the past decades and relatively recent methods as ion exchange chromatography and solvent extraction have been widely used for trace metals recovery (3–5), selective separation of metals with similar properties remains as a difficult task, especially for the $Cd^{2+}$– $Zn^{2+}$ pair. Selective separation seems to be practically impossible in the absence of complexing agents. Complexation by different ligands allowed to highlight the role of the medium and could lead to improve the separations (6).

A combination of complexation and ultrafiltration processes is one of the widely used alternative process for heavy metal separation (7–10). In complexation enhanced ultrafiltration process; metallic ions are complexed with macroligands (i.e., polymers, colloids, micelles), thus the molecular dimension of the metal ions to be separated is enlarged. Metal complex and the complexing agent can be retained by the membrane while water and non-complexed ions pass through the membrane.

In polymer enhanced ultrafiltration (PEUF), generally water soluble polymers or polymeric ligands are used. Examples of water soluble synthetic polymers used in PEUF processes are polyvinylalcohol (11,12), polyglycidyl methacrylate (13), polyacrylic acid (14), poly allylamine (15) and poly(ethyleneimine) (16).

Among the synthetic water-soluble polymers, poly (ethylenimine) (PEI) has high binding ability, because of having an unshared electron pair on the N atom which can form donor bonds with the coordination of unsaturated transition metals (17). Branchy poly(ethylenimine) (PEI) contains ethylamine as the repeating unit. The tertiary amino nitrogens are the branching points. A typical PEI of MW 60000 contains ca. 350 primary amines, ca. 700 secondary amines, and ca. 350 tertiary amines and it has chelating sites both in the main chain and side chains (18).

The performance of the ultrafiltration (UF) process is evaluated with two main criteria, which are the amount of retention of the target component by the membrane and permeate flux. Operational parameters such as pH, temperature, feed concentration, membrane type, and configuration affect the degree of retention and permeate flux and hence the performance of the process (19–21). In the (PEUF) processes, in addition to these conventional operational parameters, coefficients directly affecting polymer-metal binding characteristics can be very important

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for the process performance. The amount of metal ions free in solution and that of bound to polymer and the retention of the metal ions are strongly dependent on pH and ionic strength. The effect of pH, on the binding ability of polymers and as a consequence on the performance of the PEUF operation was the subject of various studies in literature (22–25).

The degree of dependency of the forces that direct the metal-polymer interactions on ionic strength was related with the characteristics of the bonds. Bonds may be electrostatic or coordinating bonds. In this sense, chelating polymers (i.e, PEI) may be differentiated from polyelectrolytes. Polyelectrolytes-metal interactions are generally dominated by electrostatics whereas polychetalogens formed coordinative bonds with metal ions (26,27) which are significantly more selective than ionic interactions. Although coordinative bonds with metal ions are more selective than ionic interactions it was also reported that neutral salts like sodium chloride or sodium nitrate influence the complexation of metal-polychetalogen complexation (28).

In order to understand the effect of ionic strength on the interaction of polymers in aqueous solution various studies were performed (29,30). However, such a study is difficult because the solution contains at least four components: poly ions, counterions, coions, solvent, and also different interactions like intra- and inter- chain interactions, long-range electrostatic interaction, hydrophobic interaction, and entropic force (31). In order to get accurate results every component and every interaction should be considered simultaneously.

Although an accurate model is still absent in light scattering from polymers (32), a combination of static and dynamic light scattering data give complementary pieces of information, and for this reason they are commonly used for the characterization of the polymer solutions (33,34). Different patterns of light scattered from a solvent/solute system can be measured by dynamic and static light scattering methods. In dynamic light scattering method by utilizing the real time intensities of scattered light, the diffusion coefficient, the hydrodynamic radius ($R_H$) of the particle can be estimated. Second virial coefficient ($A2$), radius of gyration ($Rg$), and molecular weight are the characterization parameters that can be estimated by utilizing the time-averaged intensities of the light scattered in the static light scattering method (35).

Although PEI is extensively used as a complexation agent for PEUF, most of those studies are for single metals and batch systems (24). In the preceding study, the effects of pH and ionic strength on the retention behavior of single metal solutions of Cd, Ni, Zn were investigated extensively by employing a continuous ultrafiltration system at a total recycle mode (36). The aim of this study is to investigate the effects of pH, ionic strength on fractional separation of Cd, Ni, and Zn from binary and multi-component mixtures of these metals. To gain insight about the characteristics of association between highly branched PEI and target metal ions and the effect of salt concentration on this association were investigated by performing dynamic and static light scattering measurements. Radius of gyration ($Rg$), hydrodynamic radius ($R_H$), and second-order virial coefficient ($A2$) of PEI macromolecule and metal-PEI complexes were estimated for different experimental conditions.

Based on the previous studies, system parameters (i.e., transmembrane pressure, temperature, membrane material, feed concentration) were all set for the optimum permeate flux (37).

## EXPERIMENTAL

### Materials

In the ultrafiltration experiments and in atomic absorption spectrometry analysis, poly ethyleneimine (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 hydroxide NaOH (Merck), nitric acid $HNO_3$ (Merck), and ultrapure water having a specific conductance of $18.3\,M\Omega cm^{-1}$ obtained from the 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.

### PEUF Experiments

Feed solutions (5 L) were prepared prior to the ultrafiltration experiments. For the preparation of equimolar binary mixtures 7.5 ppm and for ternary mixtures 5 ppm of each metal solution was used. Predetermined amounts of PEI and metal salts were separately dissolved in ultrapure water. When PEI dissolves in water, the pH of the solution becomes about 10. In order to prevent the precipitation of metals, the pH of the PEI solution was adjusted by adding $HNO_3$ and NaOH. Then the metal solution was mixed with PEI solution and stirred at 250–300 rpm for at least 2 hours to make sure that complexation equilibria between metal ions and PEI was established. The pH of the solutions was adjusted to desired values during the mixing period and during the experimental run.

In the preparation of salt containing solutions, the same procedure was applied: metal and PEI solutions were prepared separately and then mixed at optimum pH value. A predetermined amount of $NaNO_3$ was added to the metal-PEI solution and stirred at 250–300 rpm for overnight.

Amicon-Millipore SP20 ultrafiltration system has been employed with spiral wound regenerated cellulose cartridges having an effective area of $0.93\,m^2$. The equipment 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 pressure of the feed side was 13 kPa and that of the 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.

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

### 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 the 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, the 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 wad drained again and flushed with osmosized water, until the pH of the permeate stream appeared to be in neutral pH range and standard water permeate flux has been reached.

### Dynamic and Static Light Scattering Analysis

Prior to analysis, depending on the desired concentration for DLS/SLS experiments, samples were diluted and then filtered using a 0.4-mm filter, in sample cells. Static and dynamic light scattering measurements were performed by ALV/CGS-3 Compact Goniometer System simultaneously. An argon ion laser operating at a 633-nm wavelength and 35-mW output power was used as a light source. The measurements were done at 10 different angles in the range of $60^\circ \leq \theta \leq 150^\circ$ and at 25°C. For each angle three different measurements were performed and subsequently averaged. The data were normalized to absolute scale by using toluene as a reference material.

## RESULTS AND DISCUSSIONS

For the estimation of process efficiency on fractional separation of target metals, the selectivity coefficients were calculated for each binary metal mixture by the following formula:

$$S_{\frac{A}{B}} = \frac{C_{pB}/C_{fB}}{C_{pA}/C_{fA}} = \frac{1-R_B}{1-R_A} \tag{1}$$

where $C_{pA}$ and $C_{pB}$ are permeate and $C_{fA}$ and $C_{fB}$ are feed concentrations of components A and B. $R_A$ is the retention of component A, and $R_B$ is the retention of component B in the mixture. Values of $S_{A/B}$ greater than 1 indicates favorable fractional separation of A over B. Ideal selectivity coefficients were also calculated with Eq. (1) based on the retention values in single metal solutions.

## Cd-Ni BINARY MIXTURES

### Effect of pH and Loading

In Fig. 1, the retention profiles of Cd-Ni in equimolar binary mixture of these metals at pH 6.5, 6 and 4 were shown. As seen from the figure, at pH 6.5 and pH 6, depending on loading (metal/polymer ratio) 55–95% and 51–97% Ni retention was achieved respectively. Reduction of pH from 6.5 to 6 did not affect the retention of Ni however, the percent recoveries of Cd dropped from 83% to 57%. At pH 4, as seen from Fig. 1 the order of binding was changed and Ni retention became favorable over that

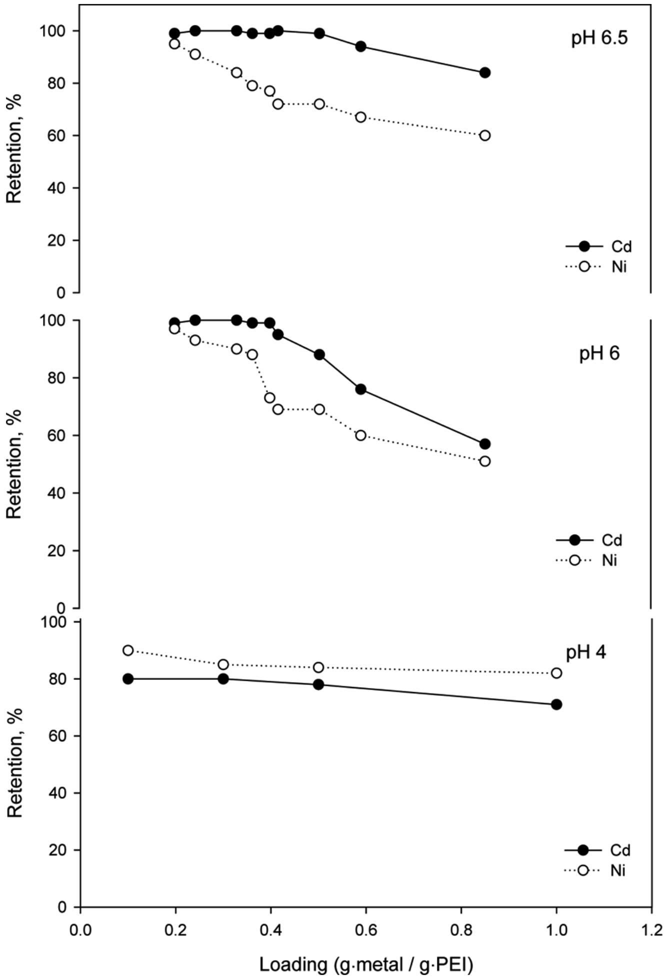

FIG. 1. Effect of pH on retention profiles of *Cd* and *Ni* in binary metal mixtures.

of Cd. This distinguishing response of the Cd-Ni pair in the presence of PEI at different pHs enables to optimize the PEUF process according to desired end products. A previous ultrafiltration study done with PAA showed that Cd-Ni fractionation was not favorable because of the poor selectivity of this chelating polymer (38), it may be concluded that for the fractional separation of the Cd-Ni pair, PEI is favorable over PAA.

To understand the effects of the co-existence of the Cd and Ni on retention, the selectivity coefficients in single ($S^{i}_{Cd/Ni}$) (36) and binary metal mixtures $S_{Cd/Ni}$ were calculated (Fig. 2). From Fig. 2, it can be seen that, $S_{Cd/Ni}$ values are far greater than $S^{i}_{Cd/Ni}$, which means that the Cd retention in the binary metal solution is much higher than its retention in a single metal solution. It can be concluded that when Ni is added into the Cd solution, nickel ions enhance the cadmium-PEI interaction and hence a higher retention of cadmium is achieved.

Favorable binding of cadmium over nickel ions may be explained as follows: All metallic ions apparently form hydrates in aqueous solution, surrounding themselves with large numbers of molecules of water. The ease with which metallic ions form hydrates increases with increasing charge and with decreasing radius (39). Since the ionic radii of nickel ions (r = 0.69A) is smaller than that of cadmium ions (r = 0.92A) (40), nickel ions tend to form hydrates more easily. Hydrolysis effects renders the Ni-PEI complexation reaction, due to the fact that the amino groups present in PEI cannot be easily bound to hydrolyzed metal ions owing to the competitive reactions between $OH^-$ ions and amino groups (41).

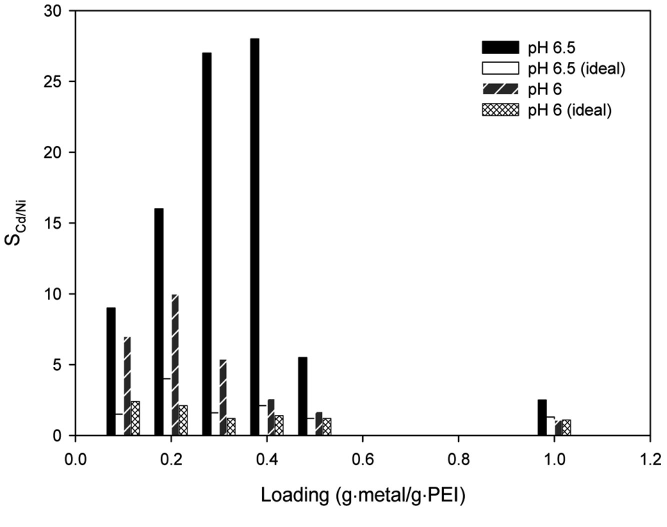

FIG. 2. Comparison of $S_{Cd/Ni}$ with $S^{i}_{Cd/Ni}$.

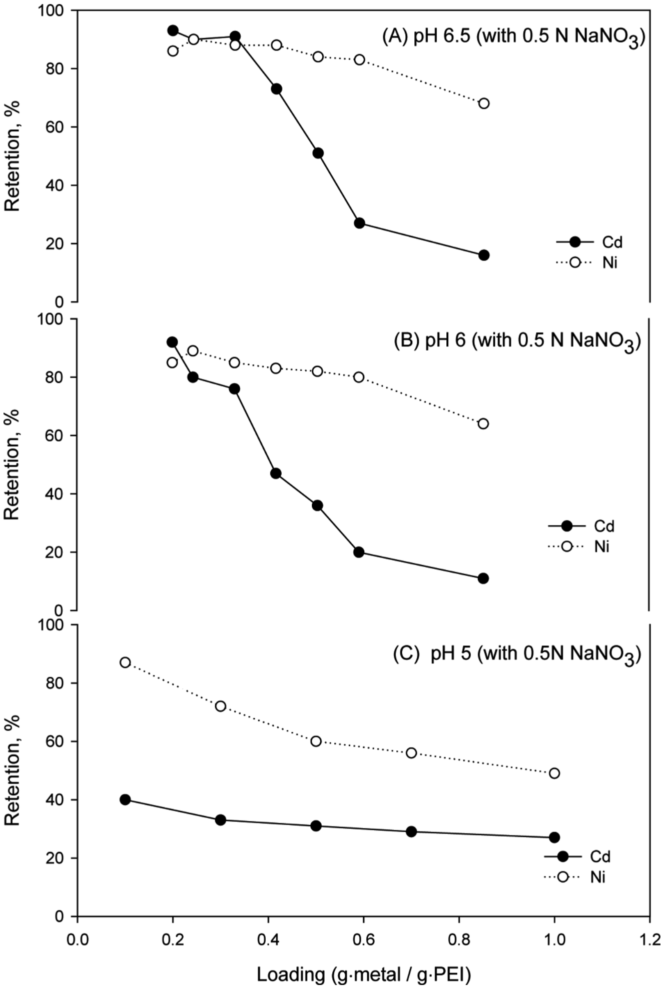

FIG. 3. Effect of ionic strength on the retention profiles of Cd and Ni in binary metal mixtures.

## Effect of Ionic Strength

As the retention profiles of Cd-Ni pair in the absence (Fig. 1) and in the presence of 0.5 N $NaNO_3$ (Fig. 3) were compared it can be observed that the addition of salt enhanced the Ni-PEI binding while depressing the binding ability of PEI with Cd. Depending on the metal/polymer ratios 9–68% reduction in the Cd retention was recorded on the contrary to the 9–15% increment in Ni retention at pH 6.5. The same behavior was also observed at pH 6 and 5; in average 40% and 47% decrement in Cd retention, 11% and 17% increment in Ni retention were achieved at pH 6 and pH 5, respectively.

It is known that the PEI molecules tend to aggregate and become smaller in the presence of high salt concentrations. Because of the aggregation of PEI particles, active sites of the macromolecule may be buried and in this way the ability to form metal complexes was inhibited. In addition, an excess amount of $Na^+$ ions coming from the dissociation of salt may also cause a deformation of the ions and hence changes the binding ability of the ions to PEI macromolecules which also became smaller in a high ionic strength medium.

Although target metals selected for this study all belonged to Group B of the periodic table and therefore eligible for deformation, the degree of deformation of the ions of these metals may be different from each other. For the Cd – Ni pair, nickel ions tend to deform more easily then cadmium ions in the presence of a distorting medium (39). Therefore when a high amount of salt was added to the solution, the distorting medium appeared in the presence of excess $Na^+$ ions deform the symmetrical structure of nickel ions. Deformed nickel ions can penetrate into the PEI macromolecule and can reach the active sites more easily than cadmium ions and hence nickel binding becomes favorable over cadmium binding in high ionic strength medium.

For Cd – Ni binary metal solutions, fractional separation of the metals can be achieved by PEUF in the presence of PEI and process can be optimized as follows—for cadmium fractionation without addition of salt, operation pH should be higher than 4. On the contrary, for nickel fractionation, operation pH should be below 4. However, such a low pH may not be preferable because of the pH sensitivity of the membranes. To fractionate Ni from solution at reasonable pH ranges ($5 \leq pH \leq 6.5$), at least 0.5 N $NaNO_3$ should be added to the solution.

## Cd-Zn BINARY MIXTURES

### Effect of pH and Loading

The effect of pH on retention profiles of Cd and Zn in equimolar binary mixture of these metals were shown in Fig. 4. As can be seen from the figure, depending on the loading values, 85–99% of Cd and Zn were retained by the membrane in the pH range of 5–6.5. However, fractional separation cannot be achieved in the presence of PEI in this pH range. To achieve selective separation, the pH of the system should be reduced down to 4. At pH 4, the PEI-Zn binding is favorable over the PEI-Cd binding and hence, Zn ions can be retained by the membrane whereas, Cd ions pass through the membrane. At pH 4, in average 45% of Cd and 65% of Zn were able to be complexed by PEI and hence retained by the membrane.

Selectivity coefficients ($S_{Zn/Cd}$) at different pHs were calculated and compared (Fig. 5) with the ideal selectivity values ($S^i_{Zn/Cd}$) which were calculated by retention data obtained in a single component mixture of Cd and Zn (36). Ideal selectivity coefficients are far greater than 1, whereas selectivity coefficients in binary metal mixtures were close to 1. This means that in a single metal solution Zn retention is higher. However, coexistence of these metals affected the metal-polymer binding equilibrium and hence the extent of retention. Because of the similar properties of these metals, separation cannot be achieved and selectivity coefficients appeared to be close to 1.

It is known that in any periodic group the stability of the hydrates is greatest for the smallest ions, while the number of water molecules normally held is greatest for the large ions (39). Cadmium and zinc are both belong to group IIB and cadmium have greater ionic radii as compared to

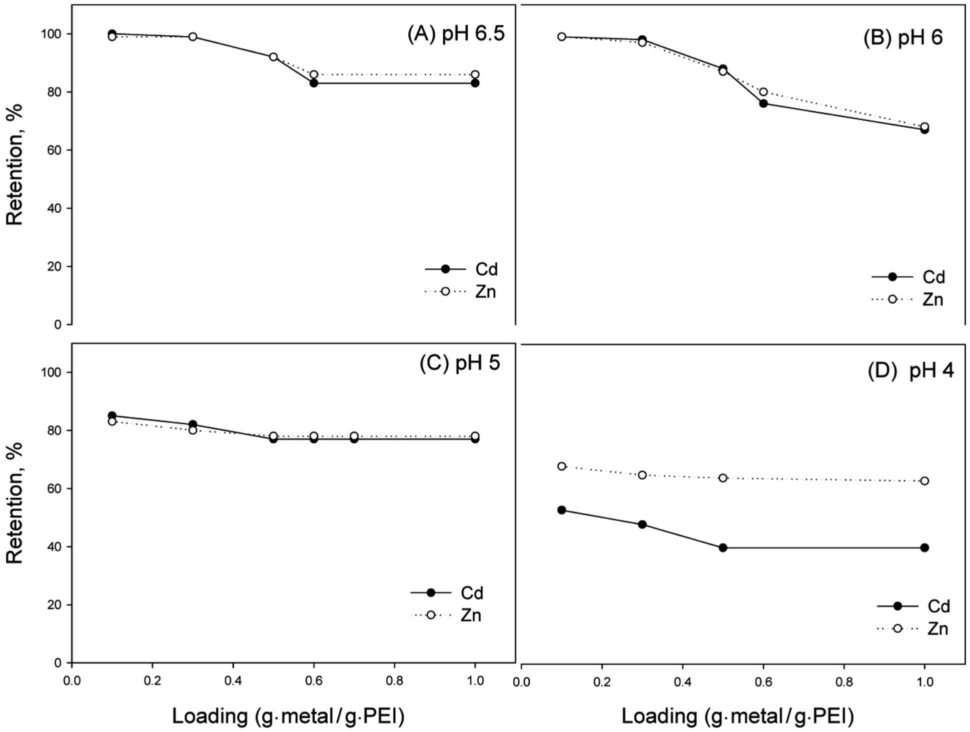

FIG. 4. Effect of pH on retention profiles of *Cd* and *Zn* in binary metal mixtures.

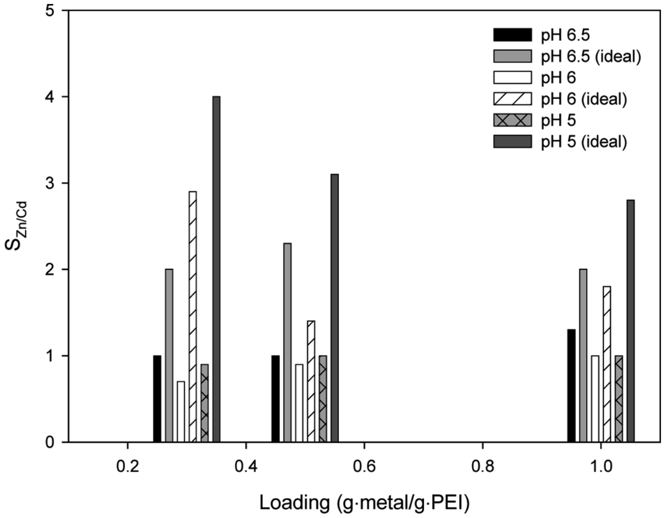

FIG. 5. Comparison of selectivity coefficients ($S_{Zn/Cd}$) in single and binary metal mixtures.

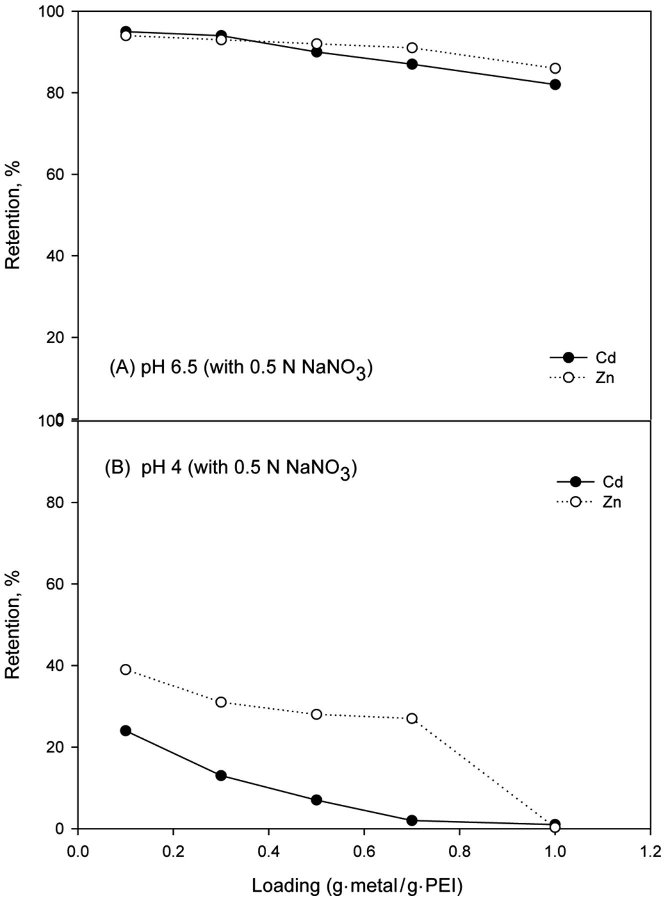

FIG. 6. Effect of ionic strength on the retention profiles of Cd and Zn in binary metal mixtures.

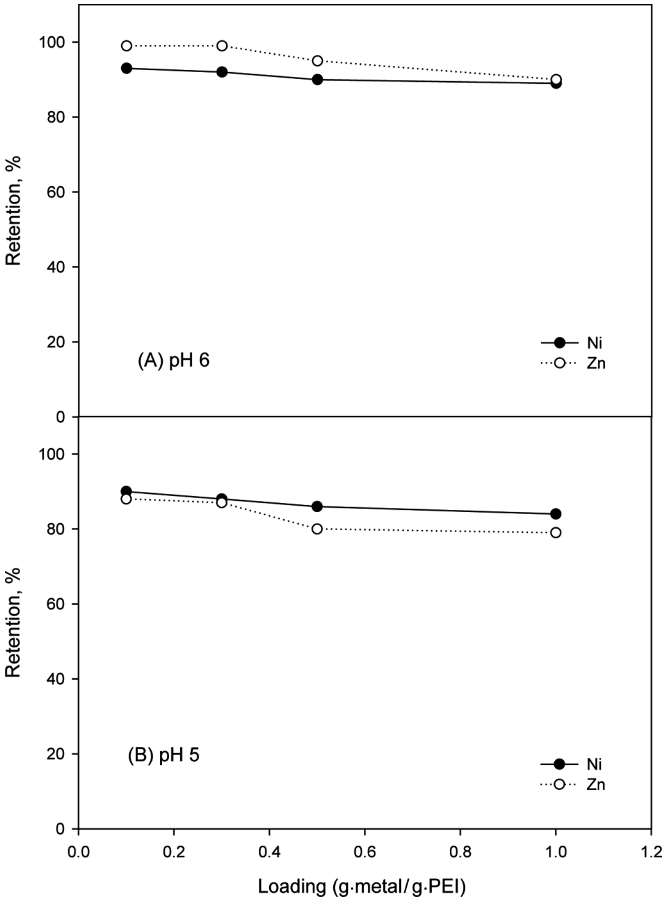

FIG. 7. Effect of pH on retention profiles of *Ni* and *Zn* in binary metal mixtures.

zinc ($r_{Cd} = 0.92A$, $r_{Zn} = 0.74A$), therefore cadmium ions assumed to hold a greater amount of water molecules as compared to zinc and as a consequence the binding ability of zinc ions was expected to be higher than that of cadmium. However, this suggestion seems to be valid only at low pH values, such that at pH 4 and 5, Zn retention become favorable; on the contrary, at high pH values the extent of retention for both metals appears to be the same.

## Effect of Ionic Strength

As shown in Fig. 6, at pH 6.5, almost complete retention of both Cd and Zn can be achieved in the presence of 0.5 N $NaNO_3$ for low loading values. Addition of salt did not affect the binding ability of these ions. This gives rise to removing both Cd and Zn from the binary component solutions even at high ionic strength, however, selective separation cannot be achieved.

On the other hand, the adverse effect of high salt concentration can be clearly observed at pH 5.5 (Fig. 6). Almost complete retention of both metals can be achieved at pH 5.5 without salt; however, with 0.5 N $NaNO_3$

maximum of only 59% of Zn and 43% of Cd was retained. By the reduction of pH down to pH 4, further decrease in recovery ratios were observed; only 28–56% of Zn and 10–25% of Cd.

## Ni-Zn BINARY MIXTURES

### Effect of pH and Loading

At pH 6 and 5, the affinity of PEI towards both of the metals was almost the same, therefore, almost the same degree of retention was obtained and more than 90% of both Ni and Zn can be recovered but selective separation cannot be achieved (Fig. 7). The same behavior was also observed in previous studies for the Ni-Cu pair. It was reported that in the presence of PEI, only pH change was not sufficient to selectively remove nickel from copper (42).

### Effect of Ionic Strength

By the addition of salt, Ni was retained more than Zn at pH 5 and 6 (Fig. 8). PEI macromolecules shrinks in high ionic strength medium, and because of the shrinking effect active sites of the macromolecule available for metal binding are buried. Nickel ions have a tendency to deform in the presence of high amounts of counterions, and by courtesy of the deformation ability they may penetrate into the active sites of the PEI molecules which was buried by the presence of excess $NaNO_3$. Therefore Ni retention became favorable over that of Zn.

Fractional separation of Ni over Zn can be achieved at pH 6 with the addition of salt. 67–94% of Ni and 39–87% of Zn can be recovered at pH 6. On the other hand, by the decrease in pH down to pH 5, the fractionation efficiency

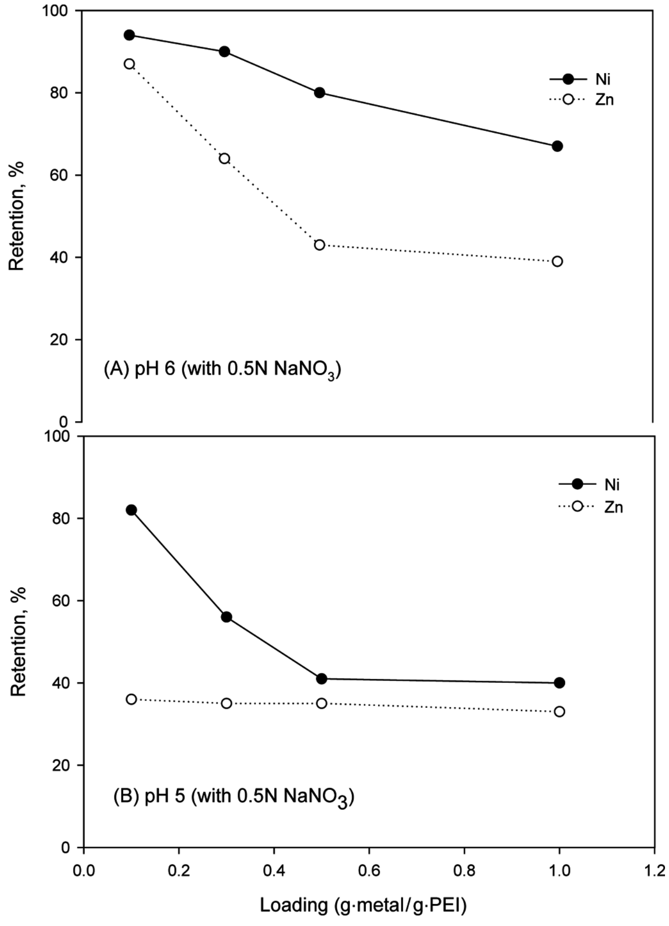

FIG. 8. Effect of ionic strength on the retention profiles of Ni and Zn in binary metal mixtures.

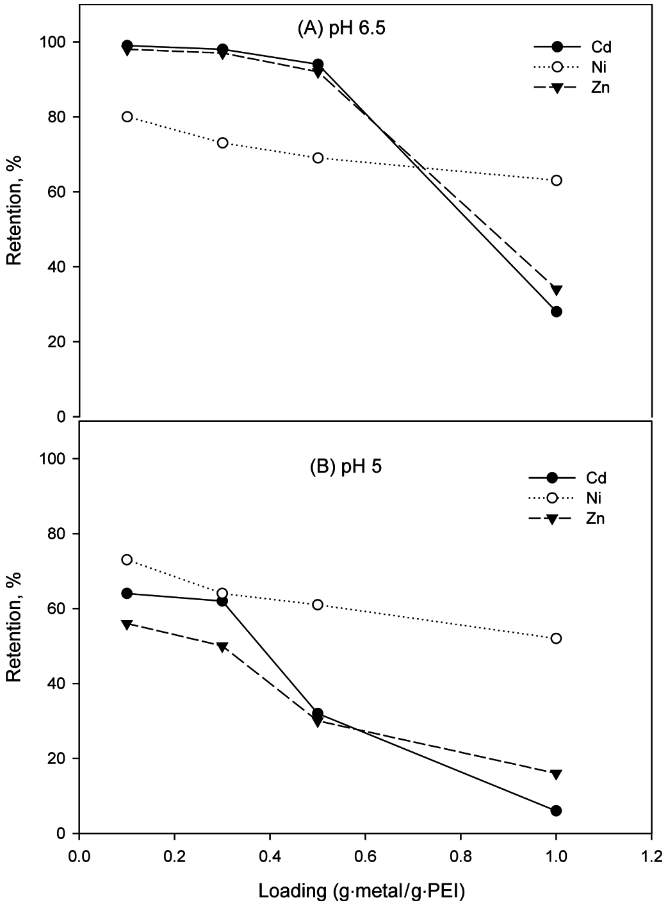

FIG. 9. Effect of pH on retention profiles of *Cd*, Ni and *Zn* in ternary metal mixtures.

TABLE 1
Light scattering data for PEI/Water solutions at different pH values

| Sample | Rg (nm) | $R_H$ (nm) | A2 ($mol \cdot dm^3/g^2$) |
|---|---|---|---|
| PEI (pH 12) | 181 | 47 | $1.0 \times 10^{-6}$ |
| PEI (pH 6) | 75 | 57 | $1.6 \times 10^{-5}$ |
| PEI (pH 4) | 49 | 55 | $8.0 \times 10^{-6}$ |

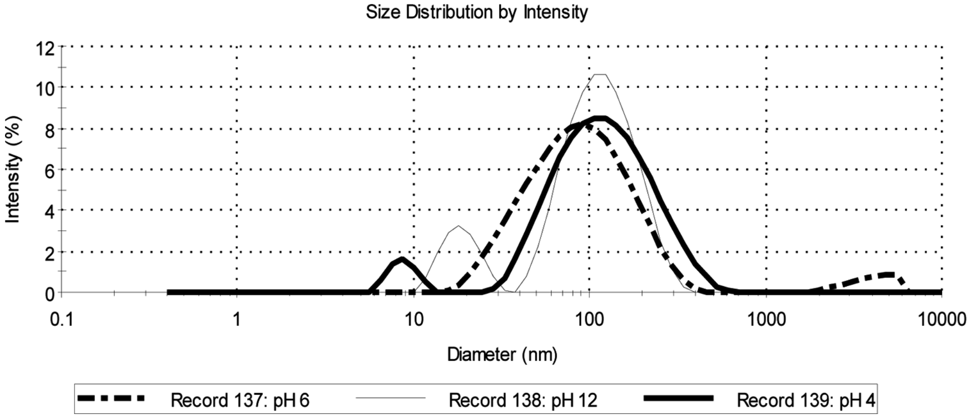

FIG. 10. Effect of pH on size distribution of PEI molecules.

was reduced and only 40–82% of Ni and in average 34% of Zn can be removed from the aqueous solution.

## Cd-Ni-Zn TERNARY MIXTURES

At pH 6.5, Zn and Cd show similar affinities towards PEI and as a consequence same amounts of Cd and Zn were able to be complexed with PEI and hence retained by the membrane (Fig. 9). Fractional separation of Cd-Zn pair over Ni can be achieved from the ternary mixture—depending on the metal/polymer ratios, 28–99% of Cd-Zn ion pair can be fractionated, and 62–80% of Ni can be removed from the solution.

At pH 6.5, the degree of binding decreases in the order of $Cd \geq Zn > Ni$, but at pH 5 situation was reversed. Steep rise in the binding of Ni was observed and binding order became $Ni > Cd \geq Zn$ (Fig. 9). By the courtesy of increased binding ability of nickel ions, 52–72% of Ni can be fractionated from the ternary metal solution.

It can be concluded that in the presence of Zn, it is difficult to fractionate zinc or its counterpart in binary metal solutions, because of the interference effects of zinc. But in the ternary metal mixtures of Cd, Ni, and Zn, the cadmium-zinc pair showed similar binding properties and by this way fractionated from Ni.

## DYNAMIC AND STATIC LIGHT SCATTERING RESULTS

### Structure of PEI with No Added Salt

The data obtained by static and dynamic light scattering measurements were processed by utilizing the governing equations of Guinier method. The parameters extracted from Guinier plots were listed in Table 1. For polyethleneimine (PEI) solutions the refractive index increment of the solution is taken as ($dn/dc = 0.2998\,cm^3/g$) which was determined in previous studies (43).

The radius of gyration ($Rg$) describes the overall spread of the molecule and is defined as the root mean square distance of the collection of atoms from their common centre of gravity. The data in Table 1 indicate that the radius of gyration (Rg) tend to decrease as the pH decreases. PEI molecules possess a globular structure, and with the decrease in pH, the amine groups on the globule become protonated and because of the increase in repulsion forces side chains opened up. On the other hand, the amine groups inside the globule tend to collapse because of the screening effects, therefore the radius of gyration decreases.

Hydrodynamic radius ($R_H$), characterizes hydrodynamic interactions, increases to some point with the decrease in pH to 6, further reduction in pH did not affect the hydrodynamic radius. Positive second virial coefficients (Table 1) showed that the pair interaction between the macromolecules is repulsive, as expected (43). The charge density of PEI increases with decreasing pH and as a consequence second virial coefficients are expected to be higher at low pHs. However, because of the highly branched structure of PEI and screening effects chains are entangled and the effects of repulsive forces were rendered as the pH was further decreased, therefore second virial coefficients became lower but remained positive at low pHs.

The effect of pH on the size distribution of PEI macromolecules was shown in Fig. 10. PEI molecules had roughly 100 nm particle diameter at the studied pH range.

TABLE 2
Light scattering data for PEI/Water solutions at different salt concentrations

| Sample | Rg (nm) | $R_H$ (nm) | A2 ($mol \cdot dm^3/g^2$) |
|---|---|---|---|
| PEI (No $NaNO_3$) | 75 | 57 | $1.6 \times 10^{-5}$ |
| PEI $+0.25\,N$ $NaNO_3$ | 57 | 41 | $1.1 \times 10^{-6}$ |
| PEI $+0.5\,N$ $NaNO_3$ | 48 | 39 | $1.4 \times 10^{-6}$ |

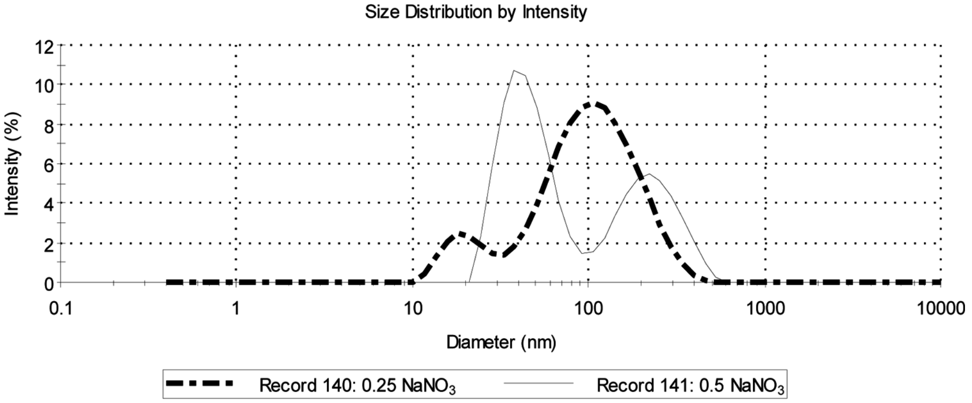

FIG. 11. Effect of $NaNO_3$ concentration on size distribution of PEI molecules.

Changes in pH affect the size distribution of PEI molecules such that; at high pH, PEI molecules form more compact complexes with narrow size distribution whereas at low pH's (pH 6 and pH 4), PEI still exhibited a mean size of $\sim$100 nm with a broad size distribution (Fig. 10).

### Structure of PEI in Presence of Salt

DLS/SLS measurements were performed for PEI solutions containing varying amounts of $NaNO_3$ salt. Experiments were performed at pH 6 and at 25°C. *Rg*, $R_H$, and the 2*nd* Virial Coefficient of the samples were estimated and tabulated in Table 2.

Electrostatic interactions between the charged particles are screened by the presence of other charged species in solution (32). In the presence of an excess of low molecular weight salt, electrostatic interactions between charges on polymer chains are screened and hence second virial coefficient ($A_2$) decreased (Table 2). A qualitatively similar dependence of $A_2$ on salt concentration was found in solutions of poly(methacrylic acid) (44) and biological polyelectrolytes (45). The general trend is that the dependence is stronger at low salt concentrations and weaker at higher salt concentrations (46).

As compared to the values obtained in the absence of $NaNO_3$, decrease in Rg (Table 2) and mean particle size (Fig. 11) were observed by the addition of $NaNO_3$. Qualitatively, the same results were obtained on other systems—carboxymethyl cellulose in NaCl solutions (47,48), partially and fully neutralized polyacrylic acid in NaCl solutions (49) and polyvinylsulphonate in KCl solutions (50). The swelling of polyions occurs at low salt concentrations because of the repulsive interactions between charges along the chain, which are screened by the presence of low molecular weight salt in the solution (51).

The dynamic/static light scattering data supports the previous observations such that at low pH's and high salt concentration, polymer conformation changes in an unfavorable manner for metal binding, therefore metal-polymer binding was rendered and reduces the removal efficiency by PEUF.

## CONCLUSIONS

From the results of this study, it can be concluded that

1. For the solutions containing equimolar mixtures of Cd and Ni, there is no inhibiting effect of one of the examined metals on complexation of the other over the range of concentrations analyzed. Thus, the removal of cadmium and nickel mixture from aqueous solutions may be conducted as effectively as the removal of each of these ions separately. $Cd^{2+}$ can be effectively separated from Ni ions at high pH values. On the other hand, a reverse case is valid at low pH values; Ni can be fractionated from the cadmium-nickel solutions. Salt concentration has a dual effect in binary metal solutions of Cd-Ni pair; by the addition of $NaNO_3$, retention of Cd ions were reduced and that of Ni ions were enhanced. Widely differing effect of ionic strength on metal retentions may be due to differences in polymer-metal interactions. By this dual effect, Ni ions can be effectively fractionated from Cd in high ionic strength medium.
2. When both Cd and Zn exist in the same solution, fractional separation cannot be achieved in the studied pH range ($5 < pH < 6.5$). Fractional separation of zinc ions from equimolar binary mixture of Cd-Zn pair can only be achieved at pH 4. High ionic strength medium did not hinder Cd-PEI or Zn-PEI complexation reactions, almost complete retention of both metals can be achieved in the binary Cd-Zn metal mixture.
3. For the Ni-Zn pair, fractional separation cannot be achieved at pH 6 and pH 5 in the absence of salt, whereas by the addition of 0.5 N $NaNO_3$, Ni can be fractionated.
4. In ternary component mixtures the pH changes the binding order of metals.

5. With the decrease in pH and salt addition, PEI molecules tend to shrink and the radius of gyration decreases and makes the PEI macromolecule unsuitable for metal binding.

## NOMENCLATURE

| | |
|---|---|
| PEI | Polyethyleneimine |
| PAA | Polyacrylicacid |
| PEUF | Polymer enhanced ultrafiltration |
| $R_H$ | Hydrodynamic radius |
| $A2$ | Second virial coefficient |
| $Rg$ | Radius of gyration |

## REFERENCES

1. Alloway, B.J. (1995) *Heavy Metals in Soils*, 2nd Ed.; Chapman and Hall: Glasgow, UK.
2. 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.
3. Agrawal, A.; Sahu, K.K. (2006) Separation and recovery of lead from a mixture of some heavy metals using Amberlite IRC 718 chelating resin. *J. Hazard. Mater.*, 133 (1–3): 299.
4. Demirbas, A.; Pehlivan, E.; Gode, F.; et al. (2005) Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on amberlite IR-120 synthetic resin. *J. Colloid Interf. Sci.*, 282 (1): 20.
5. Abollino, O.; Aceto, M.; Sarzanini, C.; et al. (2000) The retention of metal species by different solid sorbents - Mechanisms for heavy metal speciation by sequential three column uptake. *Anal. Chim. Acta*, 411 (1–2): 223.
6. Rivas, B.L.; Quilodran, B.; Quiroz, E. (2005) Metal Ion Retention Properties of Poly(acrylic acid) and Poly[N-3-(dimethylamino)propyl acrylamide-co-acrylic acid]. *J. Appl. Polym. Sci.*, 97 (3): 1385.
7. Llanoz, J.; Perez, A.; Canizares, P. (2009) Water-soluble polymer ultrafiltration process at pilot scale: Study of hydrodynamics and factors limiting flux. *J. Membr. Sci.*, 341 (1–2): 37.
8. Rivas, B.L.; Amalia, S.; Pooley, A.M. (2004) Removal of metal Ions by water-soluble polymacromonomers in conjunction with ultrafiltration membrane. *J. Appl. Polym. Sci.*, 92 (5): 2955.
9. Juang, R.S.; Shiau, R.C. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *J. Membr. Sci.*, 165 (2): 159.
10. 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.
11. Doganay, C.O.; Ozbelge, H.O.; Yilmaz, L.; et al. (2006) Removal and recovery of metal anions via functional polymer based PEUF. *Desal.*, 200 (1–3): 286.
12. Dilek, C.; Ozbelge, H.O.; Bicak, N.; et al. (2002) Removal of boron from aqueous solutions by continuous polymer-enhanced ultrafiltration with polyvinyl alcohol. *Sep. Sci.Technol.*, 37 (6): 1257.
13. Oktar, C.; Yilmaz, L.; Ozbelge, H.O.; et al. (2008) Selective mercury uptake by polymer supported hydroxyethyl sulfonamides. *React. Funct. Polym.*, 68 (4): 842.
14. Rivas, B.L.; Quilodran, B.; Quiroz, E. (2004) Trace metal ion retention properties of crosslinked poly(4-vinylpyridine) and poly(acrylic acid). *J. Appl. Polym. Sci.*, 92 (5): 2908.
15. Rivas, B.L.; Moreno-Villoslada, I. (2003) Retention of metal ions in ultrafiltration of mixtures of divalent metal ions and water-soluble polymers at constant ionic strength based on freundlich and lagmuir isotherms. *J. Membr. Sci.*, 215 (1–2): 195.
16. 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). *Desalination*, 200 (1–4): 288.
17. 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.
18. Suh, J.H. (1996). *Polymeric Materials Encyclopedia*, Salamone Ed.; CRC Press: Boca Raton, K.C., 4210 and 8230.
19. Muslehiddinoglu, J.; Uludag, Y.; Ozbelge, H.O.; et al. (1998) Determination of heavy metal concentration in feed and permeate streams of polymer enhanced ultrafiltration process. *Talanta*, 46 (6): 1557.
20. Uludag, Y.; Ozbelge, H.O.; Yilmaz, L. (1997) Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration. *J. Membr. Sci.*, 129 (1): 93.
21. Pastor, M.R.; Samper-Vidal, E. (2002) Analysis of the variation in the permeate flux and of the efficiency of the recovery of mercury by polyelectrolyte enhanced ultrafiltration (PE-UF). *Desalination*, 151 (3): 247.
22. Zambrano, J.B.; Laborie, S. (2002) Mercury removal from aqueous solutions by complexation-ultrafiltration. *Desalination*, 144 (1–3): 201.
23. Molinari, R.; Argurio, P.; Poerio, T. (2006) Ultrafiltration of polymer-metal complexes for metal ion removal from wastewaters. *Macromol. Symp.*, 235: 206.
24. Rivas, B.L.; Pereira, E.; Rocio, C.; Geckeler, K.E. (2005) Polyelectrolyte-assisted removal of metal Ions with ultrafiltration. *J. Appl. Polym. Sci.*, 95 (5): 1091.
25. Alpatova, A.; Verbych, S. (2004) Ultrafiltration of water containing natural organic matter: Heavy metal removing in the hybrid complexation ultrafiltration process. *Sep. Purif. Technol.*, 40 (2): 155.
26. Jarvis, N.V.; Wagener, J.M. (1995) Mechanistic studies of metal ion binding to water-soluble polymers using potentiometry. *Talanta*, 42 (9): 219.
27. Hamaya, T., Hiratani, K., Ohashi, K. (1994). Ultraviolet spectrophotometric studies of the reactivity of a water-soluble polymer containing pendant 8-hydroxyquinoline moieties with metal ions. *Macromol. Chem. Phys.*, 195 (8): 2739.
28. Geckeler, K.E.; Bayer, E.; Vorobeva, G.A.; Spivakov, B.Y. (1990) Water-soluble quinolin-8-ol polymer for liquid-phase separation of elements. *Anal. Chim. Acta.*, 230 (1): 171.
29. McCormick, C.L.; Nonaka, T.; Johnson, C.B. (1988) Water-soluble copolymers: Synthesis and aqueous solution behaviour of associative acrylamide/*N*-alkylacrylamide copolymers. *Polymer*, 29 (4): 731.
30. Lee, W.F.; Tsai, C.C. (1994) Aqueous-Solution Properties of poly (Trimethyl Acrylamido Propyl Ammonium Iodide). *J. Appl. Polym. Sci.*, 52 (10): 1447.
31. Sedlak, M. (1993). Domain structure of polyelectrolyte solutions: is it real? *Macromolecules*, 26 (5): 1158.
32. Sedlak, M. (1996). *Light Scattering: Principles and Development*; Oxford University Press: Oxford.
33. Galinsky, G.; Burchard, W. (1996) Starch fractions as examples of non randomly branched macromolecules. 2. Behavior in the semidilute region. *Macromolecules.*, 29 (5): 1498.
34. Normula, S.; Cooper, S. (2000) Influence of ionic content in polyurethane ionomer solutions. *J. Phys. Chem. B.*, 104 (29): 6963.
35. Kazakov, S.V.; Galaev, I.; Mattiasson, B. (2002) Characterization of macromolecular solutions by a combined static and dynamic light scattering technique. *Int. J. Thermophys.*, 23 (1): 161.
36. Islamoglu, K.S., Yilmaz, L., Ozbelge, H.O. (2009) Estimation of binding constants of Cd(II), Ni(II) and Zn(II) with polyethyleneimine (PEI) by Polymer Enhanced Ultrafiltration (PEUF) Technique. *Sep. Sci. Technol.*, 44 (11): 2559.

37. Muslehiddinoglu, J.; Uludag, Y.; Ozbelge, H.O.; et al. (1998) Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration. *J. Membr. Sci.*, 140 (2): 251.
38. Rumeau, M.; Persin, F.; Sciers, V.; et al. (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.
39. Bailar, J.C. (1956). *Chemistry of the Coordination Compounds*; Reinhold Publishing Corporation: New York.
40. 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.
41. Zhou, R.; Palmer, V.; Geckeler, K.E. (1994) Removal of inorganic ions by polymer based-colloid enhanced membrane filtration in aqueous solution. *Water Resour.*, 28 (5): 1257.
42. Molinari, R.; Poerio, T.; Argurio, P. (2008) Selective separation of copper(II) and nickel(II) from aqueous media using the complexation–ultrafiltration process. *Chemosphere*, 70 (3): 341.
43. Bastardo, L.A.; Garamus, V.M.; Bergstrom, M.; Claesson, P.M. (2005) The structures of complexes between polyethylene imine and sodium dodecyl sulfate in $D_2O$: A scattering study. *J. Phys. Chem. B.*, 109 (1): 167.
44. Ghosh, S.; Li, X.; Reed, C.E.; Reed, W.F. (1990) Apparent persistence lengths and diffusion behavior of high molecular weight hyaluronate. *Biopolymers*, 30 (11–12): 1101.
45. Morfin, I.; Reed, W.F.; Rinaudo, M.; Borsali, R. (1994). Further evidence of liquid-like correlations in polyelectrolyte solutions. *J. Phys.*, 4 (6): 1001.
46. Takahashi, A.; Kato, T.; Nagasawa, M. (1970) Electrophoresis of a rod-like polyelectrolyte in salt solution. *J. Phys. Chem.*, 74: 1980.
47. Schneider, N.S.; Doty, P.M. (1954) Macro-ions. IV. The ionic strength dependence of the molecular properties of sodium carboxymethylcellulose. *J. Phys.Chem.*, 58 (9): 762.
48. Trap, H.J.L.; Hermans, J.J. (1954). Light-scattering by polymethacrylic acid and carboxymethy1cellulose in various solvents. *J. Phys. Chem.*, 58 (9): 757.
49. Hara, M.; Nakajima, A. (1980) Characteristic behaviors of light scattering from polyelectrolyte in dilute solution region. *Polymer Journal*, 12 (10): 701.
50. Eisenber, H. (1966) Multicomponent polyelectrolyte solutions. Part IV. Second virial coefficient in mixed polyvinylsulfonate KCl systems. *J. Chem. Phys.*, 44 (1): 137.
51. Li, X.; Reed, W.F. (1991) Polyelectrolyte properties of proteoglycan monomers. *J. Chem. Phys.*, 94 (6): 4568.