Preconcentration and Remediation of Cadmium Ions with Poly (Ethylene Imine) in Conjunction with Ultra Filtration

[1]Mamta Chhabra Sharma, [2]Sandeep Kumar Sharma

[*1]Kirori Mal College, University of Delhi, Delhi, India
mamta610@gmail.com

[2]Atma Ram Sanatan Dharma College, University of Delhi, Delhi, India
sandeep259@gmail.com

Abstract – Polymer - metal interactions are of great analytical and technological interest. In this study a typical water soluble polymer PEI with amine groups at its backbone has been used to preconcentrate and remove heavy metal ions (e.g., Cd(II)) from contaminated aqueous streams using liquid-phase polymer-based retention (LPR) technique. PAUF is a membrane process based on the initial complexation of a water-soluble polymeric material. *Poly (Ethylene Imine)* PEI has been complexed with a target Cd(II) ions followed by their separation from the aqueous solution by an ultrafiltration process using polysulphone membrane. The effect of operating variables such as metal/polymer ratio and pH on retention of cadmium has been investigated. It has been established that increased pH and decreased metal/polymer loading ratio (LR) caused higher retention of cadmium. Retentions stay almost constant at a value very close to unity until a critical LR or pH value was touched.

1. Introduction

The water-soluble polymers are of abundant importance in diverse research areas e.g., environmental science, technology and biomedical field. As modified materials, they are used to remove pollutants and avoid growth of bacteria and fungi. Polymer - metal interactions are of great analytical and technological interest. Solution of water soluble polymer is an interesting two phase system. The locally high and almost constant concentration of polymeric functional groups is separated by a distance contained in a certain range. These segments of WSP containing functional moieties interact extensively with solvent and other high- and low-molecular-weight species present in the aqueous solutions. These may include other polymers thereby forming inter- and intrapolymer complexes and metal ions (e.g., (Cd(II)) forming metal polymer complexes (Sharma MC *et al* **2005, 2011;** Chatterjee SK *et al* **1992,1995a, 1995b)**. Due to these interactions, polymers in solution exhibit, beyond their chemical structure, different properties such as conformation of the polymer chains, hydrophobic interactions, surface activity or formation of higher-order structures such as aggregates, gels, etc. (Rivas,BL, *et al* **2009).** Main interaction is electrostatic type, polymer–metal ion interaction can be described by interaction of point charges and a charged surface commonly with cylindrical, spherical or ovoid geometries. Such interactions are found in many important biopolymers and synthetic polymers with many technological applications and in vivo processes, for this reason, there is great interest in the study of this kind of polymer–metal interaction (Rivas *et al* **1998a**; **1998b;** Manning GS **1984;** Hao MH *et al* **1992;** Gregor HP *et al* **1977;** Riedel C *et al* **1989;** Paoletti S *et al* **1991)**.

PAUF is a membrane process based on the initial complexation of a water-soluble polymeric material. It is the combination of two processes i.e., binding of metal ions to a water soluble polymer followed by filtration through ultrafiltration membranes. Ultrafiltration is fast emerging as a novel and multipurpose technique in preconcentration, refining, and separation processes. The pore size of these membranes ((1000-100,000 Da)) is such that heavy metals ions e.g., Cd(II), Pb(II) and Zn(II) after binding to water soluble polymers thereby forming macromolecular complexes are selectively separated. The resulting large molecule, having a larger molecular

weight than the molecular weight cut-off of the membrane, is retained, while the non-complexed ions pass through the membrane. Using water soluble polymers or tailor made new polymers by introducing new functional groups to the polymer it is possible to achieve desired results. There is no interaction between the PEI, Cd(II) ions and the membrane. However, the molecular weight cut-off of the membrane (MWCO) is smaller for separation in comparison to the molecular weight of the polymer (Volchek, K *et al* **1993**; Masse, P *et al* **1987**).

Complexation of metals with polymers takes place in the homogenous aqueous phase. In this study WSP with amine groups at its backbone has been used to preconcentrate and remove heavy metal ions from contaminated aqueous streams using liquid-phase polymer-based retention (LPR) technique (Geckeler KE *et al* **1980**; Spivakov, BYa **1985**). *Poly (Ethylene Imine)* PEI has been complexed with a target Cd(II) ions followed by their separation from the aqueous solution by an ultrafiltration process using polysulphone membrane. The metal ion i.e., Cd^{2+} selected in this investigation is because of its interest from environmental and biological points of view. Cadmium is today regarded as the most serious contaminant of the modern age. It is absorbed by many plants and sea creatures and thus presents a major problem for foodstuffs. Unlike lead, cadmium contamination cannot be removed from plants by washing them; it is distributed throughout the organism. It becomes toxic in biological environments due to its electrophilic attraction and binding to functional groups containing electron donors. This is a green technique as it is economical, does not involve harmful organic solvents, there are no harmful fumes generated and the polymers can be regenerated. Here we use environmentally benign solvent water.

The main variables on which the polymer – metal interactions depend are the pH and metal to polymer ratio. By introducing various functional groups to a given polymer, changes in the binding ability of polymer toward a target metal ion happens (Geckeler, KE *et al* **1980**; **1986**; **1990**; Shkinev, VM *et al* **1987**; Novikov, AP *et al* **1989**). Interactions of such novel polymers will be presented in the subsequently. The effect of operating parameters such as metal/polymer ratio and pH on retention of cadmium has been investigated. It has been established that increased pH and decreased metal/polymer loading ratio (LR) caused higher retention of cadmium. Retentions stay almost constant at a value very close to unity until a critical LR or pH value was touched.

There is no interaction between the PEI, Cd(II) ions and the membrane. However, the molecular weight cut-off of the membrane (MWCO) is smaller for separation in comparison to the molecular weight of the polymer (Volchek, K **1993**; Masse, P **1987**).

Molecular modeling studies using HYPERCHEM 8.2 were also performed on the polysulphone ultra filtration membrane, poly (acrylic acid) segments and Cd(II) – PAA complexes for gaining an insight into the active structures and cadmium ligand interactions.

2. Experimental

2.1 *Poly (Ethylene Imine) PEI*

PEI was supplied by BDH Chemicals Ltd (Poole, UK) in the form of 50% viscous water solution (Chatterjee *et al* **1992, 1995**).

2.2 *Cd(NO₃)₂ Cadmium Nitrate*

The $Cd(NO_3)_2$ (Merck, Stuttgart, Germany; analytical-grade) was used.

The solutions were prepared with twice distilled water, the conductivity of which was lower than $1\mu S\ cm^{-1}$.

2.3 HYPERCHEM 8.2

has been used for the molecular modeling calculations.

2.4 *Protocol for Batch Method*

A stock solution of 1.000 g/L PEI solution was prepared and equilibrated for 24 hours by keeping it on magnetic stirrer. A stock solution of 1.000 g/L cadmium was also prepared by adding 2.110 g of cadmium nitrate 1 L volumetric flask. Water was added while inverting the standard flask periodically until the solution volume reached 1 L. Stock solutions of 0.1M HCl and 0.1M NaOH were prepared by taking relevant amounts.

The polymer-cadmium feed solution was prepared in 250 mL beaker. The required volume of 1.000 g/L cadmium solution was added to the empty beaker. A 50 mL burette was then used to add water to bring the mixture volume to approximately 225 mL. 10 mL of 1 g/L of PEI solution was then added to the beaker. The beaker was placed on a magnetic stirrer to stir and equilibrate the mixture. A pH meter and drops of sodium hydroxide and hydrochloric acid were used to adjust the solution pH to within 0.01 of the desired pH (e.g., 3, 5, 7 and 9). Once the desired pH had stabilized the beaker was removed from the magnetic stirred and placed on a rotatory shaker. The solution was then equilibrated for approximately 200 rpm for two hours for the complexation reaction to complete. At the end of the two hour period the beaker was removed from the shaker and required amount was transferred to centrifuge tube fitted with ultrafiltration membrane and centrifugation was carried out. Repeated washing of retenate was done with water at feed solution pH. The feed and filtrates were analysed for cadmium ions using *Perkin Elmer Aanalyst 400 Atomic Absorption Spectrophotometer.*

The same procedure is repeated for different loading ratios and pHs.
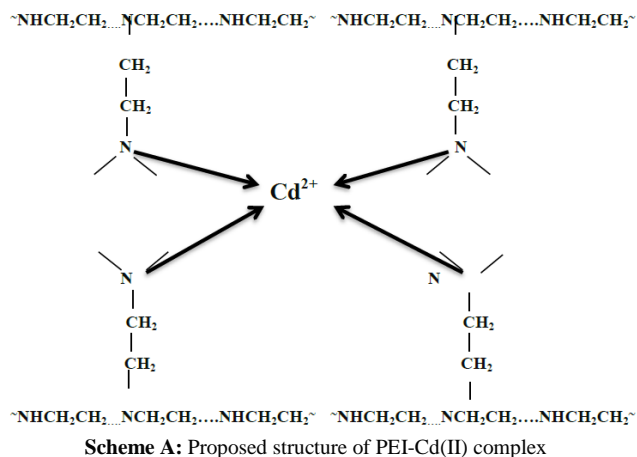
3. Discussion

The main objective of studying the effect of different factors (e.g., pH and loading ratio) in this investigation is to explore the suitable conditions for the maximum retention of cadmium.

The interactions of polymer PEI with Cd(II) ions were studied using LPR procedure. The retention values for the resulting complex were calculated from the permeate and retenate concentrations using the following equation:

$$R = 1 - \frac{c_p}{c_f}$$

where c_p is the concentration of cadmium ion in the permeate and c_f is its concentration in the feed.
The PEI-Cd(II) complex can be schematically represented as follows:

Scheme A: Proposed structure of PEI-Cd(II) complex

At the molecular level three different modes of electrostatic counterion binding may be present in these type of interactions: territorial binding, site binding and hydrophobic binding (adsorption). The counter ions present on the polymer matrix tend to be non-specifically bound to the polyion, and they are able to move along the axis of the polymer chain. If short-range, site-specific interactions are dominant, the counterions may bind on specific sites of the polyion associated with one or more charged groups. There is a competition between the ions on the matrix and cadmium ions. Apart from this weaker interactions can take place (e.g., trapping of metal ions in the polymeric bulk) (Whörle D *et al* **2003**; Rivas *et al* **2000**). This results in changes in conformation of the polymers during such interactions. Poly (Ethylene Imine) PEI may exist in two forms in aqueous solutions, neutral and protonated. As the pH increase, the concentration of neutral form increases. In its neutral arrangement, empty amine sites of PEI become available to form complexes with metal ions (Muslehiddinoglu J *et al* **1998**). In aqueous solution of PEI there is a competition between H$^+$ and Cd(II) ions for the electron pairs in the amine groups, the decrease in pH leads to strong binding of H$^+$ ions to PEI and reverse happens in case of higher pH. The effect of pH on retention of cadmium is presented in **Figure 1** and **Table 1**. The values and trends indicate that complexation behaviour of cadmium is very sensitive to pH changes and this sensitivity occurs at a higher pH range. At low pH values, replacement of protons by cadmium ions cannot be achieved which causes the low retention. For instance when the loading ratio is 0.25 the retention values are 0.76 (pH=3) and 0.95 (pH=9).
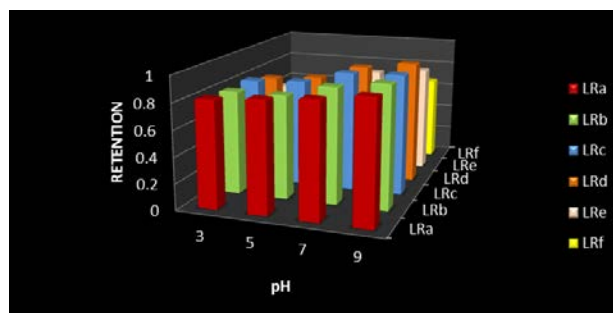

Figure1: Effect of pH on retention at different loading ratios of Cd(II)

Table1: Effect of pH on retention at different loading ratios (LR)*

pH	RETENTION VALUES					
	LR$_a$	LR$_b$	LR$_c$	LR$_d$	LR$_e$	LR$_f$
3	0.82	0.8	0.81	0.76	0.61	0.45
5	0.85	0.8	0.83	0.79	0.62	0.51
7	0.88	0.89	0.92	0.9	0.79	0.65
9	0.93	0.94	0.93	0.95	0.83	0.67

*LR$_a$=0.16; LR$_b$=0.2; LR$_c$=0.25; LR$_d$=0.33; LR$_e$=0.5; LR$_f$=1.0

The loading ration has a great impact on the metal polymer interactions. This effect has been presented in **Figures 2-5**. As a general trend a wide platform exists at very high retention values, followed by a linear decrease in the retention with the increasing LR. This behaviour is shown by polymer under all pH conditions. An interesting behaviour is exhibited at low loading ratios. Here as pH is lowered, change in retention values is more significant as compared to the behaviour at high loading ratios. This can be interpreted as follows: at lower LR there are many available sites in the polyethyleneimine structure due to high concentration of polymer. As pH decreased the competition between cadmium ions and protons increased and some of the these ions in the complexes would be replaced by protons. At high metal loading, there is a rare possibility of such a phenomena to occur. At very high pH values, there are not enough available sites to bind all cadmium ions and a high amount of free cadmium ions exist to compete with protons. Hence variation in pH results has only limited effect on retention at higher loading ratios. This effect of loading on pH sensitivity of retention is clearly presented in **Table 1**. Figure 1 clearly indicates this trend. It has been observed that variation of retention with pH is completely related to its variation with loading. Decreasing the pH resulted in a linear decrease in R values with steep slopes are obtained. Like critical loading ratio, critical pH at which decrease in retention starts, can be estimated. It is below 5 at loading 0.25.
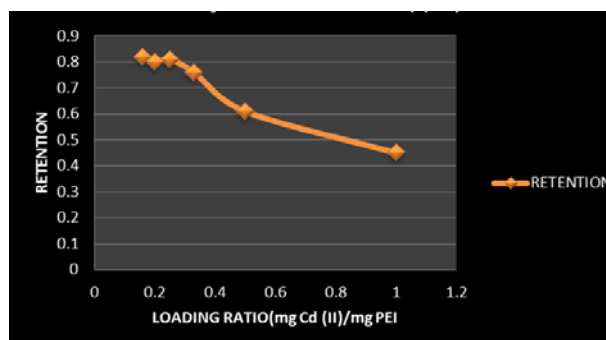

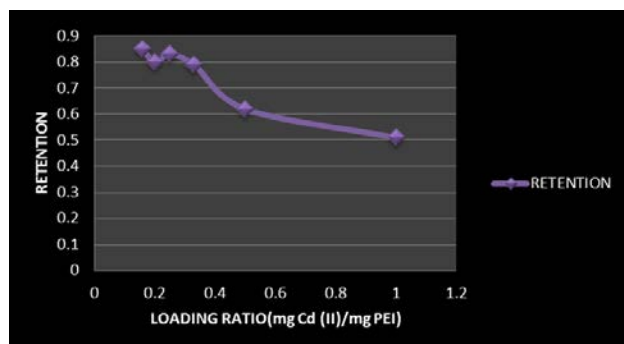**Figure 2:** Effect of loading ratio on retention of Cd(II) at pH=3

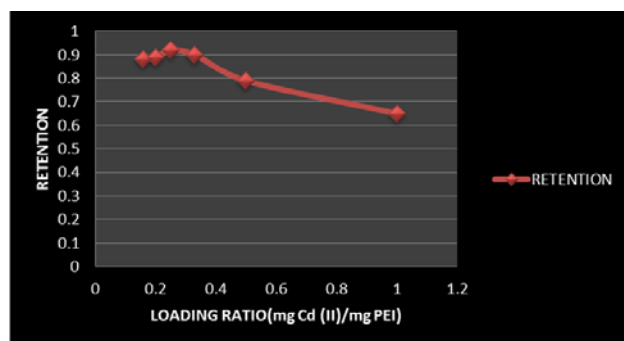**Figure 3:** Effect of loading ratio on retention of Cd(II) at pH=5

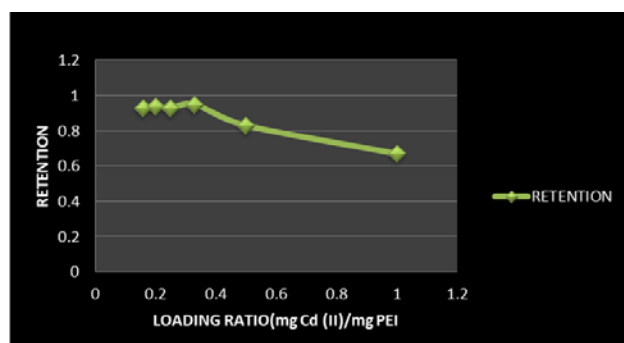**Figure 4:** Effect of loading ratio on retention of Cd(II) at pH=7

Figure 5: Effect of loading ratio on retention of Cd(II) at pH=9

3.1 Molecular modeling of Cd (II)–PEI complex

The molecular geometry of the PEI and its complex with Cd(II) was optimized by molecular mechanics (MM+) using 'HyperChem' Professional version 8.2 software (cf. **Figure 6,7**). In addition, MEP was generated from optimized minimum energy conformation of PEI and PS. **Figures 8 & 9** show the MEP for the PEI and Cd(II) – PEI complex in aqueous medium. Study of such potential map provides insight into the nature of molecular recognition in ligand – metal interaction (HYPERCHEM 8.1). The color-coded isosurface in **Figure 8** represents positive potential in green and a negative in purple color. The better chelating sites are the ones, which have relatively more electronegative MEP surface (Sharma, R. K. *et al* 2005; Pande, V. *et al* 2003).
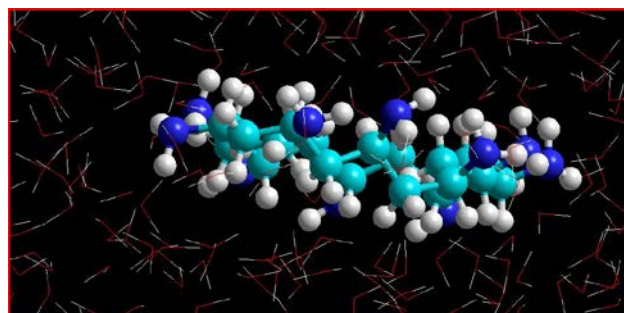

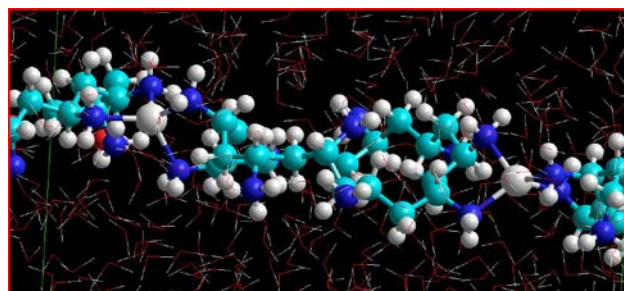**Figure 6:** Energy minimized structure of PEI in aqueous medium by MM+ method

Figure 7: Energy minimized structure of PEI – Cd^{2+} complex in aqueous medium by MM+ method.

3.2 Molecular modelling studies on Ultra filtration membrane

An ultrafiltration unit containing a polymeric ultrafiltration (e.g., polysulfone) membrane with pore sizes from 0.1 to 100 nm has been used in this study. We have used it due to its availability and low cost (Rivas, *et al* 2003).13 The chemical structure of this membrane polymer is given in figure. By studying this polymeric membrane, we can gain insight about the "working site" of the filtration on the surface. The molecular mechanics calculations on polysulphone membranes were carried out with HyperChem, release 8.1, professional version, an interactive graphic program that allows for rapid structure building, geometry optimization, and molecular display (HYPERCHEM 8.2). First of all, the structure of the membrane was minimized. **Figure 10 and 11** shows the energy minimized modeled structures of PS membrane. All the unbonded contact distances between surface atoms were calculated in order to determine if Cd(II) – PEI complexes could be reasonably well filtered on the local surface sites. As the unbonded contact distances between PS atoms is smaller than the estimated size of Cd(II) – PEI complexes, we concluded that the PS could be an appropriate membrane for our studies. This accounts for high retention of Cd(II) – PEI complexes in polymer assisted ultrafiltration using PS.
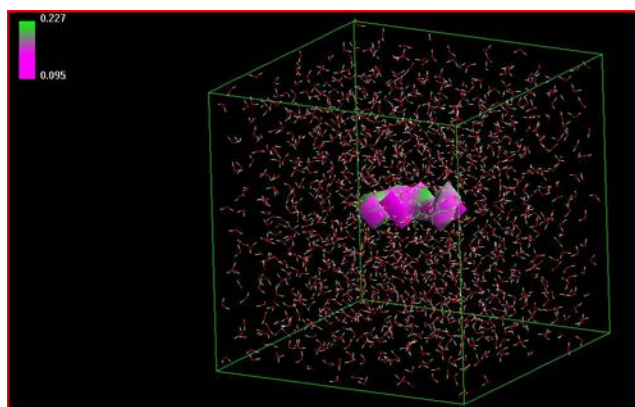
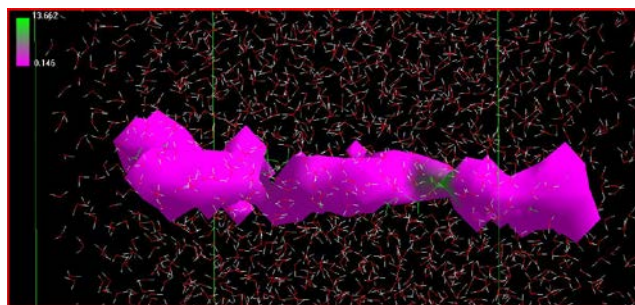**Figure 8:** 3D Mapped isosurface molecular graph of PEI

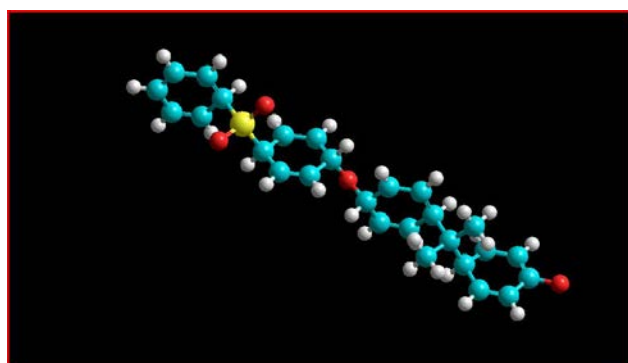**Figure 9:** 3D Mapped isosurface molecular graph of Cd(II) – PEI

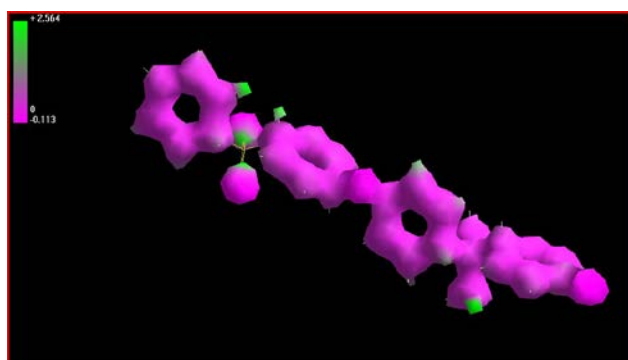**Figure 10:** Energy minimized structure of polysulfone ultrafiltration membrane

Figure 11: 3D Mapped isosurface molecular graph of polysulfone ultrafiltration membrane

4. Conclusions

The polymer assisted ultrafiltration offers a great potential for the enrichment of metal ions from water. It is inexpensive. The working conditions are easy to manipulate, and the ultrafiltration of water soluble polychelatogen complexed Cd(II) ions by PS is quantitative and reproducible. The pH and loading are the most critical parameters in PEUF process. Effects of pH and loading are contrary in nature on retention of cadmium. As the value of pH decreased retention decreased in contrast to this as the value of LR decreased the retention increased.

Acknowledgements

References

Chatterjee S.K., Chhabra, M., Johri, S.; Stability constants and related thermodynamic parameters of some quaternary intermacromolecular complexes involving polyelectrolytes and nonionic homopolymers *J. Macromol. Sci., Pure Appl. Chem.* A 32(1) (1995) 157.

Chatterjee SK, Chhabra M, Johri S " Thermodynamic studies of some complexation systems involving Methacrylic acid – acrylamide copolymer, Poly(vinyl Pyrrolidone) and Poly (Ethylene Oxide)" J. Polym. Sci:Part A: Polymer Chemistry, Vol. 32 (1994)1169-1174

Chatterjee SK, Chhabra M, Rajabi FH, Farahani BV "Thermodynamic studies on some copolymer-homopolymer-polyelectrolytre interactions" *Polymer* Vol. 33 (1992)17

Geckeler KE, Bayer E, Vorob'eva GA, Spivakov BYa, Water-soluble quinolin-8-ol polymer for liquid-phase separation of elements, Anal. Chim. Acta 230 (1990) 171.

Geckeler KE, Bayer E, Liquid-phase polymer-based retention ± a new method for separation and preconcentration of elements, Anal. Chim. Acta 189 (1986) 285.

Geckeler KE, Lange G, Eberhardt H, Bayer E, Preparation, and application of water soluble polymer-metal complexes, Pure Appl. Chem. 52 (1980) 1883.

Gregor HP, Gregor JM. Coulombic reactions of polyelectrolytes with counterions of different sizes. *J Chem Phys*;66 (1977) 1934–9.

Hao MH, Harvey SC. A lattice theory for counterion binding on polyelectrolytes. *Macromolecules* 25 (1992) 2200–8.

HyperChem, Release 8.2 *Professional Version for Windows, Molecular Modelling System,* Hypercube Inc., Canada (2010).

Manning GS. Limiting laws and counterion condensation in polyelectrolyte solutions. 8. Mixtures of counterions, species selectivity, and valence selectivity. *J Phys Chem* 88 (1984) 6654–61.

Masse P, Choe TB, Verdier A, Separation of Cu(II)±Ni(II) by a complexation±ultrafiltration method, Annali di Chimica 77 (1987) 925.

Muslehiddinoglu J, Uludag Y, Ozbelge HO, Yilmaz L Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration Journal of Membrane Science 140 (1998) 251-266.

Novikov AP, Shkinev VM, Spivakov BYa, Myasoedov BF, Geckeler KE, Bayer E, Separation and preconcentration of

actinides by a water-soluble oxine polymer using membrane filtration, Radiochim. Acta 46 (1989) 35.

Pande, V.; Sharma, R. K.; Otsuka, M.; Inoue, J.; Ramos, M. J. A molecular modeling study of inhibitors of nuclear factor kappa-B (p50)-DNA binding. *Journal of Computer-Aided Molecular Design* J. Comput.-Aided Mol. Des. 17 (2003) 825.

Paoletti S, Benegas J, Cesàro A, Manzini G. Limiting laws of polyelectrolyte solutions. Ionic distribution in mixed-valency counterions systems. I: The model. *Biophys Chem* 41(1991) 73–80.

Riedel C, Qian C, Savitsky GB, Spencer HG, Moss W. Mathematical modeling of the concentration dependence of competitive binding of counterions in polyelectrolytes. *Macromolecules* 22 (1989) 3983–6.

Rivas BL, Pereira E, Maureira A Functional water-soluble polymers: polymer–metal ion removal and biocide properties *Polym Int* 58 (2009) 1093–1114

Rivas, B.L., E.D. Pereira, I. Moreno-Villoslada. Water-soluble polymer–metal ion interactions. *Progress in Polymer Science*. 28(2) (2003) 173-208.

Rivas, B. L.; Moreno-Villoslada, I. Effect of the polymer concentration on the interactions of water-soluble polymers with metal ions. *Chem Lett* (2000) 166.

Rivas BL, Moreno-Villoslada I. Binding of Cd++ and Na+ ions by poly(sodium 4-styrene sulfonate) analyzed by ultrafiltration and its relation with the counterion condensation theory. *J Phys Chem B* 102 (1998) 6994–9.

Rivas BL, Moreno-Villoslada I. Evaluation of the counterion condensation theory from the metal ion distributions obtained by ultrafiltration of a system poly(sodium 4-styrene sulfonate)/Cd2+/Na+. *J Phys Chem B* 102 (1998) 11024–8.

Sharma MC and Sharma SK "Equilibrium And Related Thermodynamic Studies Of Hydrogen Bonded Multicomponent Complex In Mixed Solvents" International Journal of the Physical Sciences, 6(31), (2011) 7161-7165.

Sharma MC and Sharma SK " Thermodynamic and electrochemical study of multicomponent polymer complexes of varying composition" *e-Polymers*, (2005) 067.

Sharma, R. K.; Pande, V.; Ramos, M. J.; Rajor, H. K.; Chopra, S.; Meguro, K.; Inoue, J.; Otsuka, M. Inhibitory activity of polyhydroxycarboxylate chelators against recombinant NF-κB p50 protein-DNA binding. *Bioorg. Chem.* 33 (2005) 67.

Shkinev VM, Vorob'eva GA, Spivakov BYa, Geckeler KE, Bayer E, Enrichment of arsenic and its separation from other elements by liquid-phase±polymer-based retention, Sep. Sci. Tech. 22 (1987) 2165.

Spivakov BYa, Geckeler K, Bayer E. Liquid-phase polymer based retention technique: the separation of metals by ultrafiltration on polychelatogens. Nature 315 (1985) 313–5.

Volchek K, Keller L, Velicogena D, Whittaker H, Selective removal of metal ions from ground water by polymeric binding and microfiltration, Desalination 89 (1993) 247.

Whörle D, Pomogailo A. Overview and biological systems. In:Whörle D, Pomogailo AD, editors. Metal complexes and metals inmacromolecules, synthesis, structure and properties. Weinheim:*Wiley-VCH Verlag GmbH & Co KGaA* (2003) 1–24.

Curriculum Vitae

Dr Mamta C Sharma obtained a Ph.D degree in 1994 in Polymer Chemistry from Department of Chemistry, University of Delhi, India. She has been working as Associate Professor at Kirori Mal College, University of Delhi, India since 1992.She is the peer reviewer of many international journals including, Journal of Polymer Science. Her key areas are environmental issues which include use of water soluble polymers, industrial byproducts e.g., Rock phosphate, Coal Fly Ash in remediation of heavy metal ion contaminated soil and water. Her publications are in Journals and International Conferences of repute. She has authored couple of books.

Dr Sandeep K Sharma obtained a Ph.D degree in 1993 in Analytical Chemistry from Department of Chemistry, University of Delhi, India. He has been working as Associate Professor at Rajdhani College, University of Delhi, India since 1993. Presently he is Officer on Special Duty at Atma Ram Sanatan Dharma, University of Delhi. His key areas are environmental issues, Green Chemistry etc. His publications are in Journals and International Conferences of international repute.