CHAPTER 5

SUMMARY AND SCOPE FOR FUTURE WORK

5.1 SUMMARY OF WORK DONE

Polymeric chelating resins are renewable, easy to be separated and often have high adsorption capacities and hence these materials have been found to be potential adsorbents for the removal of impurities from wastewater. Therefore four new novel chelating polymeric resins bearing O, N, S and P donor atoms in the form of chelating groups in the polymer backbone has been choosen for the removal of heavy metal ions, such polymeric resins include

i) polyamides with amide, pyridyl, azomethine and thiourea moieties (PAP, PAT)

ii) polyimine containing thiodiazole and imine mioties (TDIP) and

iii) polyurethane containing urethane, shift base and thiourea moieties (PU).

The above mentioned polymers were synthesized and utilized as an effective adsorbent for removal of metal ion like Pb(II), Cu(II), Ni(II) and Cd(II) from aqueous medium. The adsorbents (PAP, PAT, TDIP and PU) were characterized using the FT-IR, $^1$H-NMR, $^{13}$C-NMR spectroscopic and XRD techniques. The thermal stability was analyzed using TGA studies. Surface morphology of synthesized and spent adsorbents was explored by
SEM analysis. The effect of various parameters such as the solution pH, adsorbent dose, contact time, initial metal ion concentration and temperature, on the adsorption of metal ions with PAP, PAT, TDIP and PU were studied in detail. Further, based on these studies, the kinetics of adsorption, adsorption isotherms and the thermodynamics of the adsorption process were also explored. In addition, desorption of the metal ions from the loaded adsorbents was also carried out to ascertain the reusability of the adsorbents. The results of the adsorption of metal ions onto the (PAP, PAT, TDIP and PU) are summarized below:

- The FT-IR analysis shows that the polymers PAP, PAT, TDIP and PU have a variety of binding sites such as amide, pyridyl, azomethine, thiourea, thiodiazole which are involved as the potential binding sites for the adsorption of metal ions onto polymeric adsorbents. The FT-IR spectrum of monomers and the polymers supports the structure of the monomers and polymers explained. Further $^1$H-NMR, $^{13}$C-NMR spectrum of PAP, PAT, TDIP and PU confirms the proposed structure of the monomers and polymers. XRD studies confirm that the polymers (PAP, PAT) are amorphous and (TDIP and PU) are crystalline. Thermal stability of the polymers (PAP, PAT, TDIP and PU) suggests that even at elevated temperatures the adsorbents can be effectively utilized. The SEM image of the PAP, PAT, TDIP and PU shows an irregular pattern and a more porous surface for metal ion adsorption.

- The solution pH is one of the most important critical parameters in the adsorption of metal ions from aqueous solutions. The pH value affects the surface charge of the adsorbent, the degree of ionization, and the speciation of adsorbate during the adsorption process. At low pH values, the
H⁺ ions occupy most of the adsorption sites on the adsorbent surface and only a small amount of metal ions could be adsorbed, because of electrostatic repulsion with H⁺ ions on the adsorbent surface. With an increase in the pH value, the adsorbent surface becomes negatively charged, and hence, the adsorption of metal ions increases and reaches the maximum at a pH value of 6.0. The decrease in the adsorption efficiency at higher pH (>6.0) may be due to the formation of metal hydroxides. It can be inferred that a pH of 6.0 is the most favourable value for metal ion adsorption.

- In the study of the effect of the adsorbent dosage on the adsorption of metal ions shows that the percentage of metal ions removed increases with an increase in the adsorbent dosage due to an increase in the adsorption sites. The maximum adsorption of metal ions was achieved with an adsorbent dosage of 60 mg/L and it reaches almost a constant value beyond 60 mg/L.

- Metal ion removal increases with an increase in the contact time and attains equilibrium after 70 min for all the metal ions studied. The pattern shows a rapid adsorption of metal ions on the external surface of the adsorbent during the initial stages and reaches a saturation value beyond the contact time of 70 minutes.

- The adsorption kinetics of metal ions onto the adsorbents were studied by using the pseudo-first order, pseudo-second order, intra-particle diffusion and the elovich kinetic equations. The kinetic results show that the metal ion-adsorbent system cannot be described by the pseudo-first order equation and the Elovich kinetic equation. Since the $R^2$ values obtained for
these equations are low, and the calculated \( q_e \) values also considerably deviate from the experimental values, the pseudo-second order equation provides the best correlation of the experimental data. It can be inferred from these studies that the chemisorption mechanism is the rate controlling step.

- The effect of initial metal ion concentration on adsorption capacity shows that there is an increase in the adsorption capacity with an increase in the metal ion concentration up to an equilibrium value. Beyond this value there is a decrease in the percentage of metal ion removal. This is attributed to the saturation of the available active sites on the adsorbent beyond a certain initial metal ion concentration.

- The equilibrium isotherm data have been analyzed by using the Langmuir, Freundlich, and Redlich-Peterson adsorption isotherms. The characteristic parameters for each isotherms and its related \( R^2 \) values have been determined. The applicability of the Freundlich, Langmuir and Redlich-Peterson isotherm equations PAP, PAT, TDIP and PU system indicate, that a monolayer adsorption and heterogeneous surface conditions exist under the studied experimental conditions. The adsorption of metal ions onto the adsorbent surface is thus complex, involving more than one mechanism. The values of the equilibrium parameter \( (R_L) \) from the Langmuir adsorption isotherm, and the ‘n’ values from the Freundlich adsorption isotherm indicate that the adsorption process is favourable for all the metals.

- With increase in the temperature the percentage removal of metal ions decreases, this is mainly due to a decrease in surface activity suggesting that the adsorption between the
metal ions and the adsorbent is an exothermic process. Thermodynamic parameters such as Gibbs free energy ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were evaluated. The results show that the adsorption of metal ions onto the adsorbents (PAP, PAT, TDIP and PU) is spontaneous and exothermic in nature. The negative value of $\Delta G^o$ indicates that the adsorption process is feasible and spontaneous. The negative value of $\Delta H^o$ reveals the exothermic nature of adsorption process. The randomness at the adsorbent-solution interface during the adsorption process is explained using the $\Delta S^o$ values.

- Desorption and regeneration studies shows that the polymeric adsorbents are most effective ones. Low concentration of 0.1 N HCl, H$_2$SO$_4$ and CH$_3$COOH serves as good recycling agents. Low concentrations of the regenerating agents suggest that recycling process is a cost-effective one. Even after five cycles of regeneration there is no serious performance decline in the efficiency of the polymeric adsorbents.

- Based on the above observations, it can be concluded that PAP, PAT, TDIP and PU have high potential towards removal of heavy metal ions from aqueous solutions. Comparing all the four adsorbents, the adsorption capacity are in the order of PU > TDIP > PAT > PAP. All four adsorbents are suitable for a wide range of initial metal ion concentrations to treat wastewater containing high metal ion concentrations.

5.2 SCOPE FOR FUTURE WORK

- The most promising technique for the removal of metal cations is their adsorption on organic adsorbents containing
chelating functional groups. The interactions between different chelating groups with different metal ions are of specific interest. The nature of interaction are generally interpreted by Lewis acid-base principle, where the chelating groups can be taken as Lewis bases while the heavy metals ion acts as Lewis acid. Metals can be adsorbed by the polymers in the pendant group or in the polymer backbone. The co-ordination bond between the metal and the polymeric ligand is an integral part of the adsorption phenomena. In the present work different polymeric chelating ligands were examined and we have suggested the formation of co-ordination bond between the polymer and the metal ions. The nature and type of the co-ordination will help in designing specific functional groups which can target the specific metal ions.

- The future work is to assign the type of co-ordination bond and the nature of the ligand formation between polymers and metal ions. There is a lot of scope in designing new polymers other than the functional groups explained in this work.

- The BET surface areas of these types of polymers are low when compared to the polystyrene cross-linked adsorbents. However, the efficiency of these polymers is much higher than the carbon-chain polymers for metal ion adsorption. Hence a detailed study on the effect of surface area on the adsorption capacity of the polymers for metal ion adsorption will be a valuable one.