CHAPTER IV
ION REMOVAL STUDIES
USING POLYMERIC LIGANDS

4.1 INTRODUCTION

The separation of metal ions present as contaminants in water is complicated by the number of variables that must be considered including the solution composition, the pH and the presence of organic substances. Although several technologies exist for the removal of metal ions from water, the most common ones are solvent extraction and ion exchange techniques. Solvent extraction\textsuperscript{156,157} involves contacting the contaminated water with an organic liquid extractant, which is insoluble in water. The extractant is capable of ion exchanging or forming chelates with the metal ion. Upon mixing, the metal ions are transported to the organic phase. The phases are allowed to separate, and the metal ions are stripped from the loaded organic phase with an appropriate solution. The concentrated metal ion solution can then be purified or disposed.

Solvent extraction offers the advantages of fast kinetics, high capacities and selectivity for target metal ions.\textsuperscript{158} The finite aqueous solubility of the extractants, solvents and modifiers is, however, a significant disadvantage.\textsuperscript{156} This not only adds to the cost of the procedure through loss of reagents, but contaminates the water with potentially toxic organics. There is also loss of the organics through evaporation and entrainment.\textsuperscript{156} In addition, solvent extraction is not
recommended for dilute metal ion solutions due to the large volumes of extractants needed.\textsuperscript{159}

Ion exchange resins operate on the same principles as solvent extraction. These resins contain functional groups capable of complexing or ion exchanging with metal ions. The resins are subjected to contact with the contaminated solution, loaded with metal ions, and then stripped with an appropriate eluent.\textsuperscript{160} Because the functional group interacting with the metal ion is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The resins can be regenerated and reused for continuous processes.\textsuperscript{161} A disadvantage of ion exchange resins is the slower kinetics compared to solvent extraction.\textsuperscript{158} However, increasing the porosity of the resin or decreasing the bead size or cross linking can help to improve the kinetics by increasing the accessibility of the polymer supported ligands to the metal ions.

Chelating polymers have many potential applications for the selective removal and recovery of metal ions from industrial waste solutions.\textsuperscript{36} The selective removal of mercury, using resins\textsuperscript{162} with thiol groups, is one such application. The main applications for the chelating polymers are based on the high selectivity of the materials for particular ions. They have been used in the preconcentration of trace elements from solutions so dilute that no analytical determinations are possible.\textsuperscript{163} Another promising new application for chelating resins is in nuclear medicine, where very short lived
isotopes must be removed quickly and selectively from mother and daughter ions. A recent example is the use of a pyrogallol-formaldehyde polymer made for the separation of $^{68}$Ga and $^{68}$Ga ions. However, in general, the commercially available resins are not quite selective enough and the few extremely selective chelating polymers discovered have not yet been made into the physical forms beads, fibers, membranes, etc., that will give the required kinetic, physical and most importantly, the economic properties required for large scale commercial isolation of individual ions. Many chelating polymers have been fabricated on a small scale into forms, membranes and hollow fibers, other than ion exchange resins in attempts to get more convenient materials for the selective separation of ions in special applications.

A series of new copper selective amino pyridine Dowex resins were designed for large scale hydrometallurgical separation of copper from its ores. Another possible large scale application of chelating resins is in the selective removal of precious metals from sea water. Selective removal of gold from sea water, although the subject of a number of patents is equally far from reality. However, the use of chelating resins from precious metal manufacturing is important. Activated carbon or various commercial anion exchange resins are now used to recover gold from such solutions, but they are very unselective and recover a mixture of metals. Very selective chelating resins such as srafion, monivex etc., with
isothiouronium structures are available and can be used to separate the anionic gold complex ions from other non precious metal ions.

There has been growing emphasis on the studies involving polymer bound ligands.170, 171 Due to the macro environment created at the coordination centre, the polymer bound ligands have considerable difference from the simple ligands. In literature, only a relatively small number of reports are available on polymers carrying multidentate ligands that completely surround the metal ions. Polyethylene imines,172 their dithio carbamates,173 carboxy methyl174 or phosphomethyl175 derivatives are the most common examples of polydentate ligands forming four chelate rings around the metal ions. The practical advantages of attaching insoluble supports are recognized and industrially exploited. Of these, catalysis and metal ion removal capacity are the most important ones. Cross linked polystyrene beads carrying amino methyl phosphoric acid groups176, 177 and imino diacetic acid groups178 have been demonstrated to be efficient in the removal of trace quantities of metal ions. Due to chelating effects, these are superior to common ion exchange resins. Poly(styrene-sulphonamides) with EDTA like chelating groups are used for the removal of transition metal ions. Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals.179-183 A large number of these complexes containing both transition and non transition metal ions and a variety of oxime ligand systems have been
reported.\textsuperscript{184-188} There is also a report on the selective removal of Pb(II), Hg(II) and Cd(II) using the schiff base ligands supported on chelating polymer resins.\textsuperscript{189}

As the concern on industrial pollution is increasing, the demand for newer method for its control is also increasing. In the present study three types of schiff base ligands supported on amino methylated polystyrene namely, salicylaldehyde schiff base, 2-nitro benzaldehyde schiff base and vanillin schiff base have been developed as promising reagents for removal of Fe(III), Cu(II) and Ni(II) respectively from solutions. The suitability of a polymeric ligand in metal ion separation depends on the nature and structure of the chelating group, kind of metal ion to be separated, molecular architecture of the polymer support and the conditions of complexation.

This chapter explains the complete analytical studies carried out to establish the above three ligands for the effective removal of the three metal ions. For each ligand studied, optimum conditions have been developed for the removal of the corresponding metal ion.

4.2 EXPERIMENTAL

The metal ion removal studies were conducted according to the procedure described under Chapter II.
4.3 RESULTS AND DISCUSSION

4.3.1 Removal of Fe(III) Using Salicylaldehyde Schiff Base Supported on Amino Methylated Polystyrene

The following studies were conducted and optimum conditions were developed for the removal of Fe(III) using the ligand.

4.3.1.1. Effect of time

Standard Fe(III) solution (30 ppm) was refluxed with a DMF (5 mL) suspension of the polymeric ligand (0.01 g) at different time intervals. The results are presented in Table 17. The concentration of Fe(III) was determined spectrophotometrically. As expected, the metal ion removal capacity of the ligand increases as the time of reflux increases. Almost 100% removal was obtained within a time span of 20 min.

4.3.1.2. Effect of pH

The original mixture has got a pH of 2.18. The pH of the mixture was changed using buffer solutions and then determinations were carried out. The results are summarized in Table 18 and Figure 28. A close examination of this table and figure reveals that the most effective removal happened at the mixing pH itself. This is an advantage of the method, as in most of the metal ion removal studies adjustment of pH of the reaction mixture has to be carried out.
4.3.1.3. Effect of metal ion concentration

The effect of metal ion concentration on the removal capacity of the reagent was studied. For a fixed amount of the ligand (0.01 g), the removal was monitored for a set of the metal ion solutions of varying concentrations. The results are shown in Table 19. A close examination of this table reveals that, at lower concentrations of the metal ion (10-30 ppm), the removal was almost complete and it was about 85% when the concentration of the metal ion solution taken was 50 ppm. Thereafter the percentage removal was decreased, due to the insufficient amount of the ligand, as expected. It can be concluded from the above discussions that an amount of only 0.01 g of the ligand is needed to achieve 100% removal of the metal ion, if the concentration of the original solution is 30 ppm.

4.3.1.4 Effect of ligand concentration

The effect of ligand concentration was studied in the range 0.0005 to 0.05 g for a solution of metal ion concentration of 30 ppm. The result presented in Table 20 explains that for a 30 ppm Fe(III) solution, the minimum amount of ligand required for about 100% removal was 0.0075 g. But on safer side 0.01 g was used uniformly.

4.3.1.5 Interference due to other ions

A complete interference study has been carried out taking different concentration of ions. The results are presented in Table 21. It is seen that the interference due to ions such as Co(II), Ni(II),

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Cu(II), Zn(II), U(VI), Na⁺, K⁺, NH₄⁺, Ca²⁺, Cl⁻, Br⁻, NO₃⁻, NO₂⁻, and CH₃COO⁻ are highly negligible. This is one of the achievements of the method because in most of the metal ion removal procedures reported in the literature, interference due to other ions is the most practical difficulty.

4.3.2 Removal of Cu(II) Using 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

Optimum conditions were developed for the removal of Cu(II) using the ligand by conducting the following experiments.

4.3.2.1 Effect of time

A known volume of standard Cu(II) solution was refluxed with 2-nitro benzaldehyde schiff base of amino methylated polystyrene suspended in DMF (5 mL) at different intervals of time. Concentration of the metal ion left was determined spectrophotometrically. From Table 22, it is clear that about 90% removal was achieved within 20 min. Hence the time of reflux was fixed as 20 min.

4.3.2.2 Effect of pH

Effect of pH on the removal of Cu(II) was studied by varying the pH of the mixture and the results are shown in Table 23 and Figure 29. Interestingly, maximum metal ion removal was obtained with the original mixture itself at the mixing pH of 4.4.
4.3.2.3 Effect of metal ion concentration

The effect of metal ion concentration was studied in the range 5 to 70 ppm with a fixed amount of ligand (0.01 g) and the results are presented in Table 24. It is found that at lower concentrations (5 to 20 ppm) less than 90% removal was achieved. With 30 ppm solution 90% removal was achieved and as the concentration of the metal ion increases, the percentage of metal ion removed decreases due to insufficient amount of the ligand. Thus for the studied amount of the ligand, the most effective removal was achieved with a metal ion solution of 30 ppm.

4.3.2.4 Effect of ligand concentration

The effect of ligand concentration was studied in the range 0.005 g to 0.1 g for a 30 ppm Cu(II) solution. From the results shown in Table 25 it is clear that the percentage of metal ion removed remains the same in the range 0.01 to 0.1 g. Hence it can be concluded that 0.01 g is the optimum mass of the ligand for achieving a 90% removal from a 30 ppm Cu(II) solution.

4.3.2.5 Interference due to other ions

A systematic interference study was carried out with foreign ions of different concentrations and the results are presented in Table 26 and 26 A. It was found that most of the ions studied, have no interfering action in the removal of Cu(II). However, Fe(III) and
Co(II) interfered severely and in fact, Fe(III) interfered even in the presence of ascorbic acid which was used as a masking agent.

### 4.3.3 Removal of Ni(II) Using Vanillin Schiff Base of Amino Methylated Polystyrene

The following studies were carried out for the removal of Ni(II) using vanillin schiff base of amino methylated polystyrene.

#### 4.3.3.1 Effect of time

A known volume of standard Ni(II) solution was taken and refluxed with the ligand soaked in DMF (5 mL) under different intervals of time. The metal ion left in the solution was determined spectrophotometrically and the results are presented in Table 27. As expected, as the time increases the percentage of metal ion removed was also increased. Within a period of 15 min. about 100% removal was achieved. Hence the refluxing time was fixed as 15 min.

#### 4.3.3.2 Effect of pH

Similar to the above two cases here also a change in the pH has got no effect in the metal removing capacity. The maximum removal was obtained with the original mixture itself. The graphical representation of the effect of pH on metal ion removal is shown in Figure 30 and the results are presented in Table 28.
4.3.3.3 Effect of metal ion concentration

The effect of metal ion concentration on the removal was studied with solutions of Ni(II) in the range 10 to 70 ppm using 0.01g of the ligand. The results presented in Table 29, reveal that at lower concentrations (10 to 20 ppm) almost complete removal of the metal ion was achieved and as the concentration increased metal ion uptake capacity decreased due to insufficient amount of the ligand. The most efficient removal occurred in the 10-30 ppm range for the studied amount of the ligand.

4.3.3.4 Effect of ligand concentration

After a certain limit there is no change in the metal ion concentration left in the mixture indicating that the ion removing capacity of the ligand is not dependent on the amount present after a fixed limit. In the present case the optimum quantity of the ligand needed for efficient removal of 20 ppm metal ion solution was 0.01 g as is clear from Table 30.

4.3.3.5 Interference due to other ions

The ions Co(II), Fe(III), Cu(II), Zn(II), U(VI), Na⁺, K⁺, NH₄⁺, Ca²⁺, Cl⁻, Br⁻, NO₃⁻, NO₂⁻ and CH₃COO⁻ were not interfering in the removal of Ni(II) using vanillin schiff base of amino methylated polystyrene. The results are presented in Table 31.
4.4 CONCLUSION

Out of the three ligands presently developed for the removal of different metals, polystyrene based schiff base ligand of salicylaldehyde gave a 100 percentage removal of Fe(III) from 30 ppm metal solution. While 2-nitro benzaldehyde schiff base is able to remove 90 percentage of Cu(II), vanillin schiff base gave a result of 100 percentage removal of Ni(II) from 20 ppm solution. The consolidated results presented in Table 32, reveal that for the removal of Fe(III), only 0.0075g of the ligand is required, while for the other two systems, 0.01g of the respective ligands are needed. The only limitation to these methods of metal ion removal is that Fe(III) and Co(II) interfere with the removal action of 2-nitro benzaldehyde for Cu(II).

It is also to be noted that all these three methods can be successfully utilized for metal ion removal, without any control of the pH.