Chapter 9

Summary and Conclusion:

The main findings of the experimental work described in Chapters 3 to 8 have been summarized below followed by the conclusions which could logically be drawn from the results of the experiments.

9.1. Summary of the Experimental Work:

The dissertation has been divided into three parts and eight chapters. The experimental portion has been described in the Part II of this dissertation. Different portions of the experimental part have been presented in Chapters 3 to 8.

Chapter 3

Chapter 3 describes the synthesis and characterisation of the quinaldinic acid amide resin. Styrene divinyl benzene copolymer beads having 8% crosslinking and of 80-100 mesh size were first nitrated using conc. H$_2$SO$_4$ - HNO$_3$ mixture to obtain nitrated polymer. The nitratet polymer was reduced to aminated polymer by tin and conc. HCl. The aminated product was finally condensed with quinaldinylnyl chloride in toluene medium in hot condition. The final product was purified by washing with methanol and water.
The resin obtained was characterised by water regain value, elemental analysis, i.r. spectra, stability towards acids, alkali, heat and γ-radiation.

Water regain value of the resin was studied and it was found out 0.37 g/g. The result of the elemental analysis showed that the nitrated polymer contains 11.31% nitrogen while the aminated polymer contains 11.46% nitrogen out of which 6.9% nitrogen is due to amino-nitrogen, and the rest is due to unconverted nitro-nitrogen. The nitrogen content of the chelating resin was found out 9.26%. Nitrogen content of the products of different steps of synthesis was determined by Duma's method. The amino group content of the aminated polymer was determined by titration in non-aqueous medium.

The i.r. spectra of the resin in a KBr matrix showed a sharp band at 1500 cm\(^{-1}\) indicating the presence of \(-\text{OONH}^-\) grouping. In addition to this sharp band four ring breathing bands were identified both in the quinaldinic acid amid resin and quinaldinic acid. The resin was found to be stable in all common acids of 4 N strength and alkali of 2 N strength at least for seven days.

From thermogravimetric and differential thermal analyses, it was found out that it was stable upto 260°C. The resin was exposed to γ-ray of different strength for different durations. The resin was stable towards γ-exposure at least upto 9.36 M. rad for 72 hr.
Chapter 4

Chapter 4 describes the general method of determination of sorption capacity of all the metal ions studied. Batch operation was performed first to determine total sorption capacity of all metal ions. In a typical batch operation a known weight (~0.5 - 0.6 g) of the resin was mixed with a known excess of the desired metal ion solution, maintained at a desired pH using suitable buffer and magnetically stirred for 24 hr to reach equilibrium. After washing the resin with the same buffer, the metal ions sorbed by the resin was eluted using appropriate eluting agent. The metal ions present in the washings and in the eluate was determined by standard methods, e.g., Atomic Absorption/Flame Emission Spectrometry, Na$_2$-EDTA titration and spectrophotometry using suitable reagents. The sorption capacity was determined in terms of mmol of metal ions sorbed per gm of the resin. The operation has been repeated over a wide pH range (0.5 to 10.0) and for different metal ions.

Sorption capacity of Na(I), K(I), Ag(I), Ca(II), Mg(II), Be(II), Zn(II), Cd(II), Hg(II), Cu(II), Ni(II), Pb(II), Co(II), Mn(II), Fe(II), Fe(III), Ce(III), Au(III), Ti(IV), Th(IV), Sn(IV) and U(VI) have been determined by batch operation. Sorption capacity was plotted against pH. The sorption capacity vs pH contours shows that Ag(I), Cu(II), Pb(II), Mg(II), Au(II) and U(VI) get sorbed in large amounts on the resin
where as Cd(II), Zn(II), Ni(II), Fe(III) and Ti(IV) get sorbed in small amounts but rest of others remain totally unabsorbed over the whole pH range studied.

The sorption patterns of Ag(I), Cu(II), Pb(II), Hg(II) and U(VI) were also studied by column operation as their absorption capacities are high and could be used for analytical purpose. A glass column of 15 cm length and 1 cm inner diameter was normally used. About 5 g of the previously swollen resin was packed to a height of 8 cm. The column was equilibrated to a definite pH by a suitable buffer and a known excess of metal ion solutions maintained at the same pH was percolated through the resin column with a flow rate of 0.5-1.5 ml/min. The resin column was washed with the same buffer and metal ions sorbed were eluted with appropriate eluting agent. Metal ions present in the washings and in the eluate was determined as stated earlier. The same procedure was repeated for all the metal ions stated earlier and for different pH values. It was found out that sorption pattern of the resin for all the metal ions are slightly smaller in a batch column than the total capacity found out in operations.

Chapter 5

Chapter 5 represents methods of study and results obtained on mercury(II). Sorption pattern of the resin for mercury(II) was determined both by batch and column operation over a
wide pH range (0.5 to 7.6). Sorption capacity increases with increasing pH of the solution reaching a maximum at pH 5.5 and then gradually decreasing. The capacity of the resin for mercury(II) at pH 5.5 was 1.98 mmol g⁻¹ for batch operation and 1.60 mmol g⁻¹ on column.

Effect of different eluents on the recovery of mercury(II) was studied. The resin sorbs mercury(II) so strongly that attempts of elution from the resin with common acids failed. Finally, the most suitable eluent was found to be 10% thiourea in 1.0 M HClO₄ recording 99.5% recovery. Mercury(II) was determined by cold vapor AAS.

Effect of volume of eluting agent was also studied. From plots of extraction (%) with different volumes of eluent it was observed that a minimum of 150 ml of eluent was required to recover 20 mg of mercury(II) sorbed on the resin column.

Mercury(II) was separated from synthetic mixtures containing one or more of the metal ions, Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Pb(II), Cu(II), Ni(II) and Fe(III).

Na(I), K(I), Ca(II), Mg(II) and Zn(II) remain practically unabsorbed by the resin hence they could be separated from mercury(II) around pH 5.0 to 6.0. Mercury(II) was also separated from Cd(II), Pb(II), Ni(II) and Fe(III) at pH 5.5. Hydrolysis of Fe(III) was prevented by adding phosphoric acid. Mercury(II) was separated from Cd(II) and Fe(III) also at
pH 2.0 because at this pH the resin has appreciable sorption capacity for mercury(II) but has no sorption capacity for Cd(II) and Fe(III). Mercury(II) was separated from Cu(II) around pH 6.5 using disodium hydrogen phosphate - citric acid buffer which suppresses the sorption of Cu(II) but has no effect on the sorption of mercury(II).

The resin has been applied for the preconcentration and separation of mercury(II) from Laboratory and Industrial waste water. The mercury(II) content of Laboratory waste water of Burdwan University was found to be 6 ng/ml and that of Industrial waste water of Durgapur city was 42 ng/ml.

Chapter 6

Chapter 6 represents the studies on uranium(VI). Both batch operation and column operation were followed to determine the sorption pattern of the resin for uranium(VI). Sorption capacity of uranium(VI) was studied in the pH range 0.5 to 4.0. The maximum sorption capacity of the resin for uranium(VI) was found out 0.32 mmol g⁻¹. The sorption capacity increases with increasing pH, becomes maximum at pH 3.7 and again decreases with increasing pH. Uranium(VI) was determined spectrophotometrically with H₂O₂ in alkaline medium. Here also sorption capacity in resin column was slightly less than the same obtained in case of batch operation.
Effect of strength of the eluted acid was studied. For this purpose 0.5 to 4.0 N HNO₃ have been tried. The result showed that extraction of uranium(VI) was above 99% when the acid was 3 N or 4 N. Hence 3 N HNO₃ have been used as eluent for all the studies on uranium(VI).

Effect of volume of the eluting acid showed that a minimum of 150 ml of 3 N HNO₃ was required to recover 15 mg uranium(VI) sorbed by the resin.

Uranium(VI) was separated from synthetic mixtures containing one or more of the metal ions Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Bi(III), Fe(III), Ce(III), Th(IV) and Ti(IV).

The resin has no affinity for Na(I), K(I), Be(II), Ca(II) and Mg(II) hence uranium(VI) was separated from these metal ions at 3.7 pH. Uranium(VI) was separated from Zn(II), Cd(II) and Ni(II) at pH 1.0 without using any masking agent, since these ions were not sorbed by the resin at this pH but uranium(VI) started being sorbed by the resin from pH ~ 1.0. Uranium(VI) was also separated from these ions at 3.7 pH using EDTA as the masking agent for these metal ions, because at this pH these ions were sorbed in small extent. Uranium(VI) was also separated from Pb(II), Ce(III), Bi(III) and Th(IV). Separation was done at 3.7 pH when uranium(VI) and Pb(II) were sorbed and other ions passed unabsorbed. Pb(II) was preferentially eluted by 0.06 M EDTA and then uranium(VI) was eluted as usual by
3 N HNO₃. Uranium was separated from Fe(III) and Ti(IV) at 3.7 pH using fluoride to prevent hydrolysis of Fe(III) and Ti(IV) and also masking them. The resin was finally used to preconcentrate and separation of uranium(VI) from uraninite ore.

Chapter 7

Chapter 7 describes studies on silver(I) and gold(III). Sorption pattern of silver(I) was determined both by batch and column operation but in case of gold(III) only batch operation was performed. Column operation was not performed because very large amount of gold(III) was required due to the high capacity of gold(III). The sorption capacity of silver(I) was studied in the pH range 0.5 to 10.0. The resin started to sorb silver(I) from pH 3.0 and sorption capacity rises with increasing pH and becomes maximum at pH 7.6 and then with increasing pH sorption capacity decreases. Maximum sorption capacity of the resin for silver(I) was found out 0.68 m.mol g⁻¹ at 7.6 pH. Silver(I) was determined spectrophotometrically using dithizone. Sorption capacity of the resin for gold(III) was determined from 4 N acidic solution to solution of pH 7.6. Maximum sorption capacity of the resin for gold(III) was found out 3.92 m.mol g⁻¹ at 1.0 pH. Gold(III) was determined spectrophotometrically using rhodamine B hydrochloride as the colorimetric reagent.
Different eluting agents were tried for silver(I) and Gold(III). Elution of silver(I) from the resin was studied with (1.0 to 4.0) N HNO₃ and with 0.5% and 5% KCN solution. Above 99.5% of recovery of silver(I) is possible with 3 N HNO₃. The resin sorbed gold(III) so strongly that its recovery from the resin was not possible with common acids even with KCN solution of 10% strength. 10% thiourea in 4 N HClO₄ was found out most effective with 99.5% recovery of gold(III).

Effect of volume of eluting agent showed that at least 150 ml of 3 N HNO₃ was required to recover 50 mg silver(I) sorbed by the resin and 150 ml of 10% thiourea in 4 N HClO₄ is required to recover 5 mg gold(III) sorbed by the resin contained in the column.

Gold(III) was separated from Na(I), K(I), Ag(I), Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II), Pb(II) and Fe(III). The maximum sorption capacity of the resin for gold(III) was 3.92 m.mol g⁻¹ at pH 1.0, where as the other metal ions started to sorb by the resin above pH 1.0. Hence separation was carried out at around pH 1.0.

Silver(I) was separated from Na(I), K(I), Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II), and Fe(III). Silver(I) was separated from Na(I), K(I), Ca(II), and Mg(II) at pH 7.6. Separation of silver(I) from Cu(II), Zn(II), Cd(II) and
Ni(II) was also effected at pH 7.6. The pH of the solution was raised upto 7.6 using \( \text{NH}_4\text{OH} - \text{NH}_4\text{NO}_3 \). Fe(III) hydrolyses above pH 2.0. Its hydrolysis was prevented by adding citrate and separation was done at 7.6 pH.

This resin was used to recover gold from dust from the streets in front of goldsmith's shops. Gold present in mud samples and silver present in rock samples were also concentrated and determined.

Chapter 8

Chapter 8 describes studies on lead(II) and copper(II). Sorption pattern of the resin for lead(II) and copper(II) was determined both by batch and column operation in the pH range 0.5 to 5.0. In both the cases of lead(II) and copper(II) sorption capacity increases with increasing pH, becomes maximum at pH 4.0 and then decreases with increasing pH. The maximum sorption capacity of the resin for lead(II) was found out to be 0.2 m.mol g\(^{-1}\) at 4.0 pH and for copper(II) 0.11 m.mol g\(^{-1}\) at the same pH. The maximum sorption capacity of the resin in a column was slightly smaller in both the cases than the value obtained in column operation.

Effect of strength of eluting acid for both lead(II) and copper(II) were studied. Nitric acid of 1 N to 4 N strength was tried for lead(II) and for copper(II), 1 N to 2 N sulphuric
acid. Besides these effect of saturated ammonium acetate containing 5% glacial acetic acid and 0.06 M Na$_2$-EDTA as eluting agents for lead(II) have also been tried. It was found out that for lead(II) 3 N HNO$_3$, saturated ammonium acetate containing 5% glacial acetic acid and 0.06 M Na$_2$-EDTA are the most effective and for copper(II) 2 N H$_2$SO$_4$ was found out to be most suitable.

Effect of volume of eluting agent for both lead(II) and copper(II) was studied. The result shows that 100 ml 3 N HNO$_3$ was required to recover 10 mg lead(II) sorbed on the resin column and 50 ml 2 N H$_2$SO$_4$ was required to recover 10 mg of copper(II) sorbed on the resin column.

Lead(II) was separated from synthetic mixtures containing one or more of the following ions e.g., Na(I), K(I), Ca(II), Mg(II), Zn(II), Mn(II), Cu(II), Ni(II), Cd(II), Fe(III), Bi(III), Ce(III), Th(IV), Sn(IV) and U(VI). Lead(II) was separated from Ce(III), Bi(III), Th(IV) and U(VI) at 4.0 pH. Here both U(VI) and lead(II) get absorbed by the resin, lead(II) was preferentially eluted with 0.06 M Na$_2$-EDTA and subsequently U(VI) was eluted with 3 N HNO$_3$. Lead(II) was separated from Na(I), K(I), Ca(II), Mg(II) and Zn(II) at pH 4.0. Separation of lead(II) from Mn(II), Fe(III), Bi(III) and Sn(IV) was also carried out at pH 4.0 but 10 ml 10% oxalate solution was added to prevent the hydrolysis of Fe(III), Bi(III) and Sn(IV). Lead(II) was separated from Cu(II), Ni(II) and Cd(II) at pH 4.0.
Here all these ions get absorbed by the resin. Lead(II) was preferentially eluted by saturated ammonium acetate containing 5% glacial acetic acid and others are subsequently eluted by 2 N H$_2$SO$_4$.

Copper(II) was separated from synthetic mixtures containing one or more of Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Ni(II) and Fe(III). Copper(II) was separated from Na(I), K(I), Ca(II) and Mg(II) at pH 4.0 by percolating the synthetic mixture through the resin column when only copper(II) sorbed by the resin and other ions passed unabsorbed. Copper(II) was eluted by 2 N H$_2$SO$_4$. Copper(II) was separated from Fe(III) at pH 4.0 in presence of fluoride to prevent the hydrolysis of Fe(III). Copper(II) was also separated from Zn(II), Cd(II) and Ni(II) at pH 4.0.

The resin have been used to separate and concentrate lead present in mud samples collected from Geological Survey of India, Calcutta.

9.2. Conclusion

The aim of the present investigation was to synthesize a chelating resin containing quinaldinic acid amide as the functional group and to characterize the resin by studying its various properties. The next step was to study the sorption patterns of various metal ions at varying pH conditions.
Finally the resin was applied to separate and concentrate these metal ions from natural samples containing these metal ions in trace quantities.

The resin was found to be stable in fairly strong alkali and all common acids and thermally stable up to 260°C. The water regain value, 0.37 g/g indicated that the resin would exhibit at least moderate sorption capacity for borderline to soft acid type of metal ions because the donor centres of the chelate group are of borderline to soft base type. As expected the sorption capacities were much higher for the soft acid type metal ions such as for silver(I), gold(III), mercury(II). Sorption capacities for borderline type metal ions were also fairly large, e.g., for lead(II) and copper(II). In addition high sorption capacity was observed for uranyl(II) a hard acid type ion, probably due to its large size.

From these studies it was concluded that the resin could be used successfully for the concentration and separation of silver(I), copper(II), mercury(II), lead(II), gold(III) and uranyl(II) ions.

In the present investigation our aim was to achieve sharp separation and concentration of traces of important metal ions from large volume of natural water or other materials.
Mercury is a very toxic metal. Direct determination of mercury in natural water samples by conventional atomic absorption spectrometry is not generally possible as the mercury contents are often below the limit of detection. So it necessitates the preconcentration of mercury(II) prior to the determination of trace or ultra-trace quantities of the metal ion in natural water. The goal was achieved by separating and concentrating trace quantities of mercury(II) present in laboratory and industrial waste water. Mercury(II) content in laboratory waste water was found out 6 ng/ml and the same in industrial waste water was found out 42 ng/ml. Hence it is clear that using this resin ppb ranges of mercury(II) can be separated and concentrated.

Uranium is another important metal of modern civilization. Uranium present in pitchblende and monazite ore only in trace quantities. Hence its preconcentration and separation prior to its determination is necessary. Uranium is generally found in association with cerium, thorium, beryllium, lead, bismuth etc. In the present investigation uranium was separated from synthetic mixtures containing these metal ions. Hence this resin could be applied for the separation and preconcentration of uranium(VI) from its natural sources where it is present in trace quantities. In the present investigation uranium was separated and concentrated from uraninite ore in which uranium content as $U_3O_8$ was in the range 0.15 to 0.17%. 
Silver and gold are also valuable metals. Their preconcentration and often their separation from other elements and also from each other is often necessary. In the present investigation microgram gold was separated and recovered from dust in front of goldsmiths shops and from mud samples. Silver was also separated and recovered from rock samples. The resin has been also successfully applied for the separation of trace quantities of lead(II) and copper(II) from synthetic mixtures. Trace quantities of lead was also separated from mud samples.

It is pointless to mention that as a prerequisite of the development of the conditions for the above mentioned applications, systematic studies on the concentration of the metal ions and their separation from normally associated elements were undertaken.

Thus, it could be prudent to conclude that the newly developed chelating ion-exchanger viz. quinaldinic acid amido styrene-DVB polymer can be used in analytical laboratories as well as industrially. The fields of application are concentration of valuable metals like gold, silver, uranium etc. from dilute solution or low grade ores for commercial purpose or for analysis. Several difficult separations are also possible. The same resin could also be used for industrial or laboratory effluents containing mercury(II) at low cost as the resin could be regenerated in all the cases.