SECTION IV
CHAPTER 10

Overall Conclusions

Abstract

This chapter describes the overall achievements of the present investigation. We have successfully synthesized three different chelating resins viz. 2-aminothiazole, dithiooxamide and 3-(3,4-dihydroxyphenyl) dl-alanine functionalized chelating resins and applied them in the separation of metal ions like Cd (II), Hg (II), Pb (II), Cu (II), Zn (II) and Pd (II). These metal ions have been separated from synthetic mixtures as well as from various environmental samples. Commercially available chelating resin viz., Tulsion-CH-90 and Chitosan derivatives CRC and CRCH have been applied in the separation of some heavy metal ions like Eu (III), U (VI) and Th (IV) using radioanalytical technique. It has to be mentioned that there still remains immense scope for various applications of all the five chelating resins which have been studied in the present work.
Overall conclusions

Our aim in the present investigation was to design, synthesize and characterize some new solid phase extractors and use them in the application of removal of toxic metal ions from microwave-assisted digested samples, to use commercially available chelating resin in the determination of heavy metal ions like europium and uranium and their separation from synthetic mixtures and to apply environment friendly chitosan derivatives in the removal of heavy and toxic metal ions like thorium and uranium as an approach towards green chemistry. Now let us summerise our achievements.

We successfully synthesized three new chelating resins and applied these in the separation of Cd (II), Hg (II), Pb (II), Cu (II), Zn (II) and Pd (II). Microwave-assisted digestion was always carried out for sample digestion. Moreover we explored the adsorption behaviour of Tulsion CH 90 and Chitosan derivatives and applied these exchangers for the separation of Eu (III), U (VI) and Th (IV).

Chapter 3 shows the adsorption behaviour of Cd (II) and Hg (II) with 2-aminothiazole resin. The maximum sorption capacity for Cd (II) is 0.15 mmol g\(^{-1}\) at pH 1 and for Hg (II) is 0.51 mmol g\(^{-1}\) at pH 6. Adsorption of metal ions is highly pH sensitive and since adsorption of cadmium and mercury takes place at different pH, separation of these two metal ions was carried out. Separation was possible in presence of foreign ions also. Taking this observation into account separation of trace amounts of Cd (II) and Hg (II) from biological samples was carried out successfully\(^1\).

In Chapter 4 the same resin has been applied to remove lead from road dust. It was seen that 2-aminothiazole functionalized resin adsorbs lead at pH 5.5. It was observed that this adsorbed metal could be easily eluted out with 2 M HNO\(_3\). The procedure was then validated with different certified samples. It was then applied efficiently in the separation of lead from road dust\(^2\).

Chapter 5 reports the synthesis of another newly synthesized chelating resin. Here dithiooxamide (DTOA) has been functionalized onto chloromethylated polystyrene divinylbezene and has been found to be very selective for copper. It also shows uptake of metal ions like Zn (II), Cd (II) and Pb (II) but much less compared to Cu (II). Evidently the reason behind the high selectivity for M (II) ions may be due to the presence of soft S and borderline N atoms. Sulfur atom plays the key role in binding the metal ions and
nitrogen helps in chelation. Thus DTOA resin has immense potentiality for removal of trace amounts of Cu (II), Zn (II), Cd (II) and Pb (II) from various matrices³.

Separation of palladium by radiotracer technique using DTOA has been discussed in details in Chapter 6. DTOA has been shown to absorb Pd (II) at pH 6. It has a $K_d$ value of 80.64 and its exchange capacity was found to be 0.1 mmol g⁻¹. Adsorbed metal ion can be completely eluted out using 1 M NH₄SCN. High purity palladium can be obtained by this method⁴.

In Chapter 7 reports the synthesis of the third newly synthesized chelating resin. Chloromethylated polystyrene-divinylbenzene has been functionalized with 3-(3,4-dihydroxyphenyl) dl-alanine (dl-DOPA). It has been used for the preconcentration and separation of Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) prior to their determination by FAAS. The maximum capacity for Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) are 0.03 mmol g⁻¹, 0.031 mmol g⁻¹, 0.056 mmol g⁻¹, 0.048 mmol g⁻¹ and 0.104 mmol g⁻¹ respectively at pH range 4.5 – 6.0. The resin can be very effective for separation of lead from digestate of different environmental samples. Nevertheless, the resin has also been successfully used for the separation of Ni (II), Co (II), Zn (II) and Cd (II)⁵.

Chapter 8 describes the separation of europium and uranium from synthetic mixtures using Tulsion CH 90 resin⁶. The maximum sorption capacities for Eu and U were found to be 0.31 mmol g⁻¹ at pH 5.3 and 0.96 mmol g⁻¹ at pH 3.1 respectively. The $K_d$ values for Eu and U are 1304 and 4890, respectively at pH 6. The uptake of $^{137}$Cs and $^{85,89}$Sr by Tulsion CH 90 resin was studied but it was found that the uptake was very low which suggests marginal or no interference. Hence the resin can be very effective for the preconcentration and separation of europium and uranium from different nuclear wastes. The method is simple, rapid and very effective for the determination of trace amounts of europium and uranium.

In Chapter 9 biopolymer chitosan derivatives CRC and CRCH have been used as solid phase extractors for several radionuclides⁷. The uptake values were of the following trend: $\text{UO}_2^{2+} > \text{Th}^{4+} > \text{Am}^{3+} > \text{Eu}^{3+} > \text{Sr}^{2+} > \text{Cs}^{+}$ for both the sorbents. The $K_d$ value of U with CRCH was found to be 384.22 and that with CRC is 125.39. More than 97 % elution of uranium was possible from the CRCH resin using Na₂CO₃. EDTA was used for >95 % elution of Th. This work suggests that biopolymers such as chitosan, especially after...
radiation grafting can be used for the uptake of U with a reasonable uptake capacity. In spite of slow kinetics chitosan derivatives are used in this work for their biodegradable property in order to minimize the use of hazardous chemicals.

There exists a common drawback for all these chelating resins. In spite of the high selectivity of these solid phase extractors towards various metal ions, they have a low sorption rate. This slow kinetics limits the application of column experiments at low flow rate conditions. Since chelation reactions are slower compared to ordinary ion exchange processes this limitation can be overcome by using longer exchange columns so that sufficient time is provided for chelation of metal ions. Higher degree of recovery for the desired metal ions can be achieved by choice of proper experimental conditions.

Literature survey shows that chelating resins containing dimethylglyoxal bis-(4-phenyl-3-thiosemicarbazone), lysine, polymeric amine etc. are being used as stationary phase in high performance liquid chromatography (HPLC) columns. There is scope for the resins we have developed to be used in the same manner due to their high selectivity for various metal ions.

To conclude, it can be said that due to the simplicity in chemical procedure and measurement techniques involved, these resins can be used to explore the unknown possibilities of many other separation problems in future.
References