SUMMARY AND FUTURE SCOPE

7.1 Summary

This chapter summarizes highlights of the results described in the thesis. Four compounds such as PAMAM dendrimer, Xanthate functionalized PAMAM dendrimer (XFPD) chelating agents, PAMAM-styrene divinyl benzene (solid supported PAMAM dendron) and DGA functionalized PAMAM-SDB chelating resin were synthesized. The potential application of the above dendrimer/dendron based chelating agents for the removal of actinides and other radionuclides from aqueous medium were explored.

Studies on ultrafiltration (UF) of uranium and thorium through regenerated cellulose acetate membrane reveal that removal of about 76-97 % of U(VI) and Th(IV) was achieved at pH 5-7. The removal of U(VI) and Th(IV) is mainly due to adsorption/mass deposition on the membrane surface. The water soluble PAMAM dendrimer chelating ligand had shown greater ability to bind with U(VI) and Th(IV) metal ions at pH > 5. These metal ions get concentrated in the retentate and adsorption/mass deposition on the membrane surface was significantly reduced. About 3 mg of G₃-NH₂ dendrimer is required for retaining 5 mg of U(VI) and Th(IV) in the retentate at pH 6. The required quantity of PAMAM chelating ligand was further decreased with increase in dendrimer generation. It is estimated that about 1.1, 0.6 and 0.45 g of PAMAMG₃, PAMAMG₄ and PAMAMG₅ dendrimers are required to retain 1g of uranium and thorium in the retentate at pH 6. Formation of various metal ion species due to hydrolysis as a function of pH plays an important role on effective complexation and selective separation. The presence of PAMAM dendrimer chelating ligand does not prevent hydrolysis of metal ions whereas the hydrolyzed metal ion species are effectively binding with PAMAM dendrimer. The binding of uranium and thorium with PAMAM dendrimer is effective at pH > 5 and in case of Eu(III) and Co(II)
effective binding occurs only at pH > 8. Hence, PAMAM dendrimer shall be employed for selective and collective removal of metal ions by adjusting the pH of the aqueous solution. Removal of U(VI) and Th(IV) from SNLW at pH 5.5 found to be greater than 90% where as other metal ions are less than 40%. At acidic pH (≤ 3), the binding of metal ions with PAMAM dendrimer was observed to be insignificant and hence PAMAM shall be regenerated.

Studies on adsorption of U(VI) and Th(IV) on indigenously developed PAMAMG3-SDB chelating resin reveals that adsorption capacity of PAMAMG3-SDB is dependent on contact time, pH and initial concentration of metal ions. The maximum adsorption of thorium on PAMAMG3-SDB was observed at pH > 5 whereas in case of uranium it is between pH 5-8. Kinetic study shows that the adsorption process is fast and equilibrium is reached within 60 minutes. Adsorption follows pseudo-second order kinetics and Langmuir isotherm model suggesting chemical adsorption. Adsorption capacity of the chelating resin increases exponentially with increase in dendron generation. PAMAMG5-SDB has adsorption capacity (qe) of 493 and 261.5 mg g⁻¹ for U(VI) and Th(IV) respectively. Study on effect of temperature on adsorption of U(VI) and Th(IV) metal ions reveals that adsorption of uranium on PAMAMG3-SDB is endothermic whereas adsorption of thorium is exothermic. The nature of adsorption (endothermic or exothermic) also depends on the metal ion speciation. The chelating resin shows more than 98% adsorption of U(VI) and Th(IV) even at high ionic strength. The adsorbed U(VI) and Th(IV) can be easily desorbed from resin by decreasing the pH of the solution and maximum of about 99% desorption was observed at pH 1 which indicates the advantages of regeneration/reusability of the resin.

Diglycolic acid functionalized PAMAM dendron- styrene divinylbenzene (DGA-PAMAM-SDB) chelating resin is observed to be effective in removal of U(VI) and
Th(IV) metal ions from both aqueous and nitric acid medium. The adsorption capacity \( (q_e) \) depends on contact time, acidity of feed solution, concentration of metal ions and temperature. This chelating resin showed superior adsorption capacity compared with PAMAM dendron of same generation. The adsorption capacity of DGA-PAMAMG\(_5\)-SDB for U(VI) and Th(IV) are about 682 and 544 mg g\(^{-1}\) respectively. At pH 3-4, Th(IV) shows > 65 % of adsorption due to stronger complexation with DGA groups. On the other hand, U(VI) shows significant adsorption only above pH > 4. Hence, the separation of U and Th from each other at lower acidic region (pH 3-4) is feasible by using DGA-PAMAMG\(_3\)-SDB. Study on effect of temperature on adsorption of U(VI) and Th(IV) metal ions reveals that adsorption of uranium on PAMAMG\(_3\)-SDB is exothermic whereas adsorption of thorium is endothermic. The percentage desorption of U(VI) and Th(IV) from DGA-PAMAMG\(_3\)-SDB resin were determined to be ~99 % and 78 % at pH 0.1 M and 0.3 M respectively.

Xanthate Functionalized PAMAM Dendrimer (XFPD) ligand is effective in removal of various metal ions from aqueous solution by precipitation. XFPD form water insoluble complexes with copper, cobalt (representative of radioactive divalent transition metal ions) and europium (representative of lanthanides & surrogate of americium) metal ions. The pH of aqueous solution plays an important role on both complexation and settling of suspended metal-xanthates. XFPD ligand effectively removes metal ions at pH > 4 and settling of suspended metal-xanthate complexes at pH > 6 requires further addition of a coagulating agent like aluminium sulphate. The presence of alkaline earth metal ions in aqueous waste enhances removal of metal ions by coagulation process. The loading capacity of XFPD for copper, cobalt and europium metal ions are determined to be 0.355 g, 0.48 g and 0.94 g and per gram of XFPD respectively. Studies on removal of various metal ions from SNLW by xanthate process showed that except cesium, all other
metal ions are effectively removed. The removal of lanthanides (Ce, Gd, La, Nd, Sm) and actinides (Th & U) are greater than 99 % and removal of Co, Ni and Zn metal ions are greater than 90 %. Transition metal ions are precipitated as metal-xanthate complex whereas lanthanides get precipitated as metal-oxo-xanthate complexes. In case of actinides, removal is due to precipitation as hydroxides as well as adsorption on metal xanthate complexes. Though alkaline earth metal ions (Ba & Sr) do not form any precipitate with XFPD ligand, their percentage removal is observed to be about 50-70 %. This could be explained by considering their role as coagulating agent. Studies with radioactive liquid waste (RLW) show that percentage removal of radionuclides are observed to be in the following order; Zr ≈ Eu ≈ Co (> 99.8) > Ce (98.84) > Sb (83.31) > Ru (79.44) > Mn (54.29) > Cs (24.02). Hence, XFPD ligand possesses potential application in decontamination of radioactive wastes.

### 7.2 Scope for the future study

In the present study, potential application of dendrimer based chelating agents in removal of radionuclides from wastewater is explored. Though, PAMAM dendrimer based chelating agents shows selectivity in removal of actinides from aqueous solution, their synthesis involve number of steps that is time consuming and expensive. Hence, attention shall be provided for reducing the number of steps involved in dendrimer synthesis.

Preparation of PAMAM dendron-SDB chelating resin finds application in both pre-concentration and waste volume reduction. The present study demonstrates the selective removal of uranium and thorium from SNLW by batch experiment using PAMAM-SDB chelating resin. However, the practical applicability of this chelating resin has to be evaluated by column experiments. DGA-PAMAM-SDB is able to remove uranium and thorium metal ions from both aqueous and nitric acid medium. Studies can
be expanded for removal of these metal ions and other actinides such as plutonium and americium from HLW. Dendrimer based chelating agents could find potential applications for treatment of various types of liquid wastes (HLW, ILW and LLW). Therefore, studies shall be extended to examine the radiation stability of these chelating agents.

Radionuclides such as $^{137}$Cs and $^{90}$Sr are the major radionuclides present in LLW arising from nuclear industry. Removal of both radionuclides demands modification in dendrimer terminal with suitable chelating groups. Removal of these metal ions may be attempted by combined precipitation method by using copper/zinc ferrocyanide, calcium phosphate along XFPD precipitating agent.

Application of indigenously developed PAMAM dendrimer chelating ligand, PAMAM dendron grafted - styrene divinyl benzene (PAMAM-SDB) chelating resin, Diglycolamic acid functionalized -PAMAM dendron- styrene divinyl benzene (DGA-PAMAM-SDB) chelating resin and Xanthate Functionalized Dendrimer (XFPD) for removal of various toxic organic and inorganic compounds in drinking water shall be explored.

Functionalized PAMAM dendrimers are bio-compatible and extensively studied as a drug delivery agent. Hence, studies shall be extended by using them as radionuclide decontamination agents.