Chapter-6
DECONTAMINATION OF RADIOACTIVE WASTE BY PRECIPITATION USING XANTHATE FUNCTIONALIZED PAMAM DENDRIMER (XFPD) CHELATING AGENT

6.1 Introduction

Decontamination of radioactive waste (i.e. removal of all radionuclides from waste) will significantly reduce the volume of waste which is important criteria in management of radioactive waste. Precipitation is one of the best suited method for decontamination of liquid wastes generated in nuclear industries. A wide range of precipitants and mixture of precipitants are being employed to improve overall decontamination. Hydroxides, carbonates, peroxides, sulphides, sulphates, phosphates and copper/nickel ferrocyanides are useful precipitants for removal of radionuclides [5, 95]. These precipitants are effective in removal of radionuclides at pH ≥ 8. Studies carried out with SNLW by using indigenously developed PAMAM, PAMAMG₃-SDB and DGA-PAMAM-SSB reveal that decontamination process is effective at pH ≥ 12. The above processes require addition of large quantity of alkali and control of solution pH. It is reported that chelating agents such as xanthate (R-OCS₂⁻) and dithiocarbamate (R-NHCS₂⁻) form complexes with various metal ions at pH > 3 [124, 154]. Xanthate complexes of copper, nickel, cobalt, iron, platinum, palladium, chromium, zinc, arsenic, mercury, antimony, bismuth and lead have been reported [155-165]. Owing to low solubility product and high stability constant of metal-xanthate complex, the xanthate chelating agent has been used for removal of heavy metal ions from wastewater [166]. In comparison with other precipitation processes, xanthate treatment offers the following advantages; i) high percentage of metal removal, ii) less sensitivity to pH variation, iii) less sensitivity to coexisting complexing agent, iv) improved sludge dewatering property and v) capability for selective removal of metals [154].
Molecules with single and multiple xanthate groups have been widely used for effective removal of heavy metal ions. Molecules with multiple xanthate groups exhibit excellent binding capacity and better settling behaviour [124, 167]. Hence, it is desirable to increase the number of xanthate functional group in a molecule to enhance binding and precipitating abilities. In recent years, xanthate functional groups have been introduced in macromolecules to increase its capacity and removal efficiency [168, 169]. Dendrimer macromolecules are choice of our interest and definite number of desired functional groups can be introduced at the periphery by exploiting the reactivity of terminal groups.

In the present work, xanthate functional groups were introduced in first generation hydroxyl terminated PAMAM dendrimer. This xanthate functionalized PAMAM dendrimer (XFPD)-PAMAMG1OCS$_2$ was used for the removal of metal ions such as copper, cobalt (representative of radioactive divalent transition metal ions) and europium (representative of lanthanide ions & surrogate of americium) from aqueous solution by precipitation. The effect of pH and ionic strength on removal of the above metal ions was studied. The settling time of precipitate as a function of time and loading capacity of XFPD as a function of metal ion concentration were investigated. Toxicity Characteristics Leaching Procedure (TCLP) and Semi-Dynamic Leaching Test (SDLT) were conducted to investigate the metal leachability and stability of metal-XFPD complex. The indigenously developed XFPD chelating ligand was deployed for the treatment of Radioactive Liquid Waste (RLW) and results are discussed in this chapter.

6.2 Experimental

6.2.1 Removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions from aqueous solution

Stock solutions of Cu$^{2+}$, Co$^{2+}$, Eu$^{3+}$ metal ions (1 g/L) and XFPD (2.7860 mM) chelating agent were prepared. Precipitation studies were carried out individually with various concentrations (25, 50, 100, 250 and 500 mg/L) of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions
by adding 0.5 mL of 2.7860 mM XFPD ligand. The resultant precipitate was filtered through whatmann 542 ashless filter paper and washed with distilled water for three times. The precipitate was dried at 343 K in a vacuum oven. The metal-XFPD precipitate was characterized by FT-IR, XPS and SEM-EDS spectroscopy. The concentration of cobalt in filtrate was determined by measuring absorbance at 520 nm using Nitroso-R salt. The concentration of europium and copper metal ions was determined using ICP-OES. Effect of pH on removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions were studied by varying the pH between 3.0 and 9.0. The pH of feed solution was adjusted by adding either 0.1 M HNO$_3$ or 0.1 M NaOH.

The percentage removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions at various pH were calculated by using the following equation 6.1.

$$\%R = \left(\frac{C_f - C_{fi}}{C_f}\right) \times 100$$  \hfill (6.1)

Where, $C_f$ is the concentration of metal ion in feed and $C_{fi}$ is the concentration of metal ion in filtrate.

Metal ion removal efficiency depends on effective complexation and its settling. Suspended particles of metal-XFPD complexes could be removed from aqueous solution by centrifugation or filtration or sedimentation process. Among these, sedimentation process is generally used for solid–liquid separation which involves settling of suspended particles. Therefore, the settling behaviour of XFPD complex of Cu, Co and Eu was studied by measuring residual turbidity of the solution as a function of time.

The influence of electrolytes such as Ca(NO$_3$)$_2$ and NaNO$_3$ on quantitative removal of metal ions was investigated. Experiments were carried out by varying the concentrations of electrolyte from 0.01M to 0.5 M with constant metal ion to XFPD mole ratio.
6.2.2 Extent of binding of metal ions

The extent of binding (EOB), number of moles of metal ion complexed per mole of XFPD, of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions as a function of their concentration was studied. About 9 ml of metal ion (Co$^{2+}$/Cu$^{2+}$/Eu$^{3+}$) solution was mixed with 1 ml of 2.786 mM XFPD solution in 50 ml centrifuge tube. The resultant precipitate was centrifuged, washed with water, dissolved in concentrated HNO$_3$ and made upto 25 ml in a standard flask. This solution and the filtrate were analyzed to estimate loaded metal ion on XFPD ligand. The EOB was calculated by using the following equation 6.2

\[
EOB = \frac{[C_M]}{[C_{XFPD}]}
\]  

(6.2)

Where, $[C_M]$ is the concentration of metal ion (Co$^{2+}$/Cu$^{2+}$/Eu$^{3+}$) complexed with XFPD (mol L$^{-1}$) and $[C_{XFPD}]$ is the concentration of XFPD in solution (mol L$^{-1}$).

6.2.3 Leaching test of Co-XFPD precipitate

The metal-XFPD precipitate was subjected to toxicity characteristics leaching procedure (TCLP). TCLP (USEPA, 1986) test is meant for classifying materials as hazardous or nonhazardous [166]. A mixture of solid precipitate and 0.1 M acetic acid at a liquid-to-solid ratio of 20:1 was equilibrated at 30 rpm in an orbital shaker at room temperature for 18 h. The leachate was filtered through a whatmann filter paper and the filtrate was analyzed for metal ion concentration.

In addition to TCLP test, a series of semi-dynamic leaching test (SDLT) using acetic acid and sodium hydroxide solutions as leachant were conducted to examine the metal ion leachability and stability characteristics of the metal-XFPD complex in simulated landfill environment [166]. Samples were collected at seven days interval for 30 days and concentration of metal ions in leachate was determined. In SDLT, equilibration of the precipitate was continued for 30 days with three sets of leachants such
as acetic acid (pH 2.5 & 6.0) and NaOH solution (pH 11.0). During the test, the liquid-to-solid ratio was maintained as 100:1.

6.2.4 Removal of metal ions from liquid wastes

Studies on removal of metal ions from simulated nuclear waste (SNLW) and radioactive liquid waste (RLW) were carried out using XFPD ligand. The preparation procedure and composition of SNLW & RLW are given in Table 2.1 of chapter 2. The performance of XFPD ligand in SNLW was evaluated by adding required amount of XFPD ligand into 20 ml of SNW taken in a 50 ml centrifuge tube. The percentage removal was calculated by determining concentration of metal ions in the filtrate using ICP-OES and AAS. Similarly, experiment with RLW was carried out by adding required quantity of XFPD into 10 ml of RLW taken in a 20 ml glass tube. The resultant suspended particles were allowed to settle for an hour and the residual activity in the supernatant was measured using HPGe detector. The percentage decontamination (% D) of each metal ion was calculated by using the following equation 6.3.

\[
%D = \frac{A_i - A_f}{A_i} \times 100
\]

Where, \(A_i\) and \(A_f\) are activities (dps) of metal ions in feed solution and supernatant respectively.

6.3 Results and Discussion

6.3.1 Complexation of Cu\(^{2+}\), Co\(^{2+}\) and Eu\(^{3+}\) metal ions with XFPD

A dark-brown precipitate was obtained by the addition of XFPD ligand to Co\(^{2+}\) and Cu\(^{2+}\) solution. FTIR spectrum of Cu-XFPD complex are shown in Fig. 6.1 (a & b). The appearance of vibrational peaks in the region of 1250-850 cm\(^{-1}\) depicts the presence of xanthate group. The peaks appear at 1049 cm\(^{-1}\) and 1197 cm\(^{-1}\) are attributed to asymmetric and symmetric vibration of \(-\text{CS}_2^+\) group. In addition,
\[ \Delta \nu(\nu(CS_2)_{asym} - \nu(CS_2)_{sym}) \] value can also illustrate the coordination fashion of the complex [123, 170]. The \( \Delta \nu \) value \( [\nu(CS_2)_{asym} - \nu(CS_2)_{sym}] \) is 148 cm\(^{-1}\), almost similar to the corresponding sodium xanthate value \( (\Delta \nu = 139 \text{ cm}^{-1}) \), which in turn suggests that XFPD ligand adopts a unidentate coordination mode in this complex (Fig. 6.2(a)). In case of Co-XFPD complex, asymmetric and symmetric stretching vibrations of \(-CS_2^-\) group gives peaks at 1203, 998 cm\(^{-1}\) and \( \Delta \nu \) value \( [\nu(CS_2)_{asym} - \nu(CS_2)_{sym}] \) is 205 cm\(^{-1}\), much larger than the corresponding sodium xanthate values \( (\Delta \nu = 139 \text{ cm}^{-1}) \). Therefore, it is expected that coordination of xanthate groups with Co\(^{2+}\) metal ion could be in tetradeative fashion (Fig. 6.2(d)).

![FTIR Spectra of (a) Cu-XFPD, (b) Co-XFPD and (c) Eu-XFPD complexes](image)

**Fig. 6.1** FTIR Spectra of (a) Cu-XFPD, (b) Co-XFPD and (c) Eu-XFPD complexes

![Coordination pattern of xanthate ligand](image)

**Fig. 6.2** Coordination pattern of xanthate ligand (a) unidentate (b) anisobidentate (c) co-ordination with two hetero atom (d) anisotetradentate
SEM images of Cu-XFPD, Co-XFPD and Eu-XFPD complexes are shown in Fig.6.3. The morphology of the particles is observed to be irregular size in the range of 20-60 µm.

The elemental analysis of Cu-XFPD complex by EDS analysis indicates the presence of copper and sulfur (Fig.6.3) with weight and atom percentages as Cu-23.2%, S-22.4% and Cu-6.7%, S-12.8% respectively. From the above percentages, the calculated mole ratio of S to Cu is about 2:1. This mole ratio depicts coordination between one copper ion and two sulfur atoms. The mechanism of complexation could be explained as follows. The Cu$^{2+}$ ion might be reduced to Cu$^{+}$ ion by xanthate group with the formation of dixanthogen (PAMAMG$_1$(OCS)$_2$) and cuprous Cu-XFPD complex expressed below (equation 6.4).

\[
PAMAMG_1OCS_2^- + Cu^{2+} \rightarrow PAMAMG_1(OCS)_2^- + PAMAMG_1OCS_2Cu\]  (6.4)

![Fig.6.3 SEM-EDS spectra of Cu-XFPD, Co-XFPD and Eu-XFPD complexes](image-url)
The mechanism has been supported by XPS analysis. The XPS spectrum of Cu2p from Cu-XFPD complex is shown in Fig.6.4 (a). Two major peaks at binding energies of 932 and 953 eV are the characteristics of cuprous xanthate signal [166] and the absence of cupric xanthate (absence of satellite structure at binding energies of 944 and 963 eV in the (Fig.6.4 a) suggests that xanthogenate unit (R-O-CS₂) coordinated with Cu⁺ ion and thus cuprous form of xanthate complex (Cu-XFPD) is precipitated. Similar result was reported by Q. Chang et al [156]. Hence XPS analysis, reveal the presence of cuprous species in the Cu-XFPD complex.

![Fig.6.4 XPS spectra of Cu2p & Co2p from Cu-XFPD and Co-XFPD complexes](image)

XPS spectrum of Co2p from Co-XFPD complex is also shown in Fig.6.4 (b). The appearance of satellite peak at 785.7 eV (2p₁/₂) along with main peak at 780.2 eV (2p₃/₂) suggests the presence of Co²⁺ ion [23]. The elemental analysis of Co-XFPD complex by EDS indicates the weight and atom percentage of cobalt and sulfur (Fig.6.3) as Co-18.48 %, S-38.54% and Co-7.27%, S-27.97% respectively. The calculated mole ratio of S to Cu is about 4:1, which depicts that four sulfur atoms are coordinated with one cobalt ion. Hence, one Co²⁺ ion is coordinated with four sulphur atoms (Fig.6.2).
In case of Eu$^{3+}$, a pale yellow precipitate of Eu-XFPD complex is formed and EDS spectrum shows the presence of europium and sulphur elements (Fig.6.3). The weight and atom percentage of europium and sulfur in Eu-XFPD complex are found to be Eu-56.84%, S-3.12% and Eu-10.91%, S-2.84% respectively. The low weight percentage of sulfur in Eu-XFPD complex is due to elimination of carbon disulphide (CS$_2$) from XFPD ligand during complex formation. According to Hard Saft Acid Base (HSAB) principle, the hard acid Eu$^{3+}$ ion interacts strongly with hard base ‘oxygen’ as compared to soft base ‘sulfur’. Hence, the coordination ability of europium with oxygen is stronger than that of sulfur atom [172]. Due to this oxophilic character of Eu$^{3+}$ ion, some of the xanthate groups in XFPD ligand dissociate with the elimination of CS$_2$ group resulting existence of only few xanthate coordinations in Eu-XFPD complex. The presence of xanthate group in europium complex was confirmed from the appearance of vibrational peaks at 1197 cm$^{-1}$ and 998 cm$^{-1}$ corresponding to asymmetric and symmetric stretching vibrations of –CS$_2$ group (Fig. 6.1c). The $\Delta\nu$ [\nu(CS$_2$)$_{asym}$– \nu(CS$_2$)$_{sym}$] value (199 cm$^{-1}$) is much larger than the corresponding sodium xanthate value ($\Delta\nu = 139$ cm$^{-1}$) and hence, it is expected that xanthate groups may coordinate with Eu$^{3+}$ ions either in anisobidentate state or by coordination with two hetero atom fashions [123, 170] as shown in Fig.6.2. It is well known that Eu$^{3+}$ exists in various chemical forms such as Eu$^{3+}$, Eu(OH)$_2^{2+}$ and Eu(OH)$_2^{3+}$ in aqueous solution at pH 3-8 and hence various types of coordination might be possible in Eu-XFPD complex. In Fig. 6.1(c), the appearance of strong vibrational peaks at 3419 cm$^{-1}$ and 1420 cm$^{-1}$ are due to O–H stretching and bending vibrations suggesting the presence of hydrolyzed europium species such as Eu(OH)$_2^{2+}$ and Eu(OH)$_2^{3+}$ in the complex.

The following types of possible complexation (equation 6.5-6.8) are predicted based on the above results.
XPS study supports the above complexation mechanism. The influence of chemical environment on binding energy (BE) values for core level photoelectron peaks of O1s and Eu4d is shown in Fig. 6.5. The shape of O1s signal is quite different for Eu-XFPD, when compared to other Eu(III) compounds reported by Mercier et al [173]. An intense peak appears at lower BE (531.1 eV) and a shoulder at high BE (531.6 eV) depicts various chemical environments of O1s in Eu-XFPD complex. The shoulder peak at high BE (531.6 eV) may be attributed to C-O of alcoholic group coordinated to Eu(III) and the peak at lower BE (531.1 eV) is attributed to C-O-C of xanthate group coordinated to the Eu(III). The same trend is found for the Eu4d peak (Fig. 6.5). Again, various coordination of Eu(III) in Eu-XFPD complex have an influence on BE values of Eu4d. The peaks at 135.2 eV and 136.4 eV are attributed to BE of Eu(III) coordinated to the xanthate ((OCS$_2$-Eu(OH)) and alcoholic (C–O–Eu(OH)) groups respectively. Finally, simultaneous study of O1s and Eu4d core level photoelectron peaks allows to discriminate between various Eu(III) coordinations in the complex.

Fig.6.5. XPS spectra of O1s and Eu4d from Eu-XFPD complex
The coordination of europium with XFPD ligand is also confirmed by fluorimetric study. Fluorescence emission spectra of free Eu$^{3+}$ and Eu-XFPD complex are shown in Fig.6.6. The emission spectra reveals well-known bands of europium luminescence corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (580 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (593 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (617 nm) transitions. Electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) at 617 nm is observed to be stronger than magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) at 593 nm, which indicates lower symmetry around Eu$^{3+}$ ions. The so called “hypersensitive” $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is very sensitive to the surrounding microenvironment of Eu$^{3+}$ ion and its intensity enhances due to complex formation with ligands [139]. Thus, the strong emission band at 617 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) clearly indicates the coordination between Eu$^{3+}$ and XFPD ligand.

![Fluorescence emission spectra of Eu$^{3+}$ and Eu-XFPD complex](image)

**Fig.6.6** Fluorescence emission spectra of Eu$^{3+}$ and Eu-XFPD complex

### 6.3.2 Effect of pH on complexation and metal ions removal efficiency

XFPD ligand could remove metal ions from aqueous solution quantitatively. The metal ion removal efficiency depends on formation of metal–XFPD complex followed by its settling. The pH of feed solution plays an important role on both formation of complex and settling of precipitate. The variation in percentage removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ ions as a function of pH is shown in Fig.6.7. At pH < 3, the ligand undergoes
decomposition by acid hydrolysis which suggests that pH of the feed solution must be maintained above 3. The percentage removal all the above metal ions increase with increasing pH between 3 and 5 beyond that it remains almost constant. At pH > 3, the xanthogenic acid groups of XFPD ligand ionize to negative xanthogenic acid radicals which enhance chelation between the XFPD and metal ions resulting increase in percentage removal of metal ions. At pH > 8, precipitation of Eu$^{3+}$ ions as europium hydroxide (Eu(OH)$_3$) occur predominantly than Eu-XFPD complex formation. Hence effective removal of metal ions using XFPD ligand shall be carried out between pH 3 and 8.

![Fig.6.7 Effect of pH on removal of Cu, Co and Eu metal ions](image)

6.3.3 Settling time of suspended particle

Studies on settling behaviour of metal-XFPD complexes as a function of time shows that Eu-XFPD complex possesses a favourable settling rate and the turbidity of the solution gets reduced by a factor of 14.6 within an hour (Fig. 6.8). In case of Co-XFPD and Cu-XFPD complexes, the settling time is highly pH dependent. At pH < 5, the precipitate has favourable settling speed whereas at pH > 6, the colloidal suspensions of Co-XFPD and Cu-XFPD complexes were not settling down by gravity for reasonable length of time. The suspended particles do not aggregate into larger particles due to
similar charges associated with the complex [167]. It is also observed that these suspended particles settle down by the addition of coagulating agent like aluminium sulphate. The turbidity of Co-XFPD and Cu-XFPD colloidal solutions was reduced by a factor of 7.2 & 7.5 within one hour by addition of aluminium sulphate. Hence, about 2-3 h is sufficient for settling of metal complexes after the addition of XFPD ligand and coagulating agent.

![Graph](image)

**Fig.6.8** Residual turbidity of complexes as a function of time

### 6.3.4 Extent of binding of Eu$^{3+}$ and Cu$^{2+}$ metal ions

The extent of binding of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions with XFPD ligand as a function of metal ion concentration is shown in Fig. 6.9. It is observed that loading of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ ions increases with increasing concentration of metal ions and gets saturated at mole ratio of 12.3, 10 and 10.4 respectively. The higher loading capacity of XFPD ligand may be attributed to coordination of these metal ions with amine, amide and xanthate groups present in the XFPD ligand. From this EOB studies, a typical loading capacity for Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions were determined to be 0.355 g, 0.48 g and 0.94 g per gram of XFPD respectively. All subsequent experiments were carried out with the above mole ratios at pH 5.
Fig. 6.9 Extent of binding of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions with XFPD ligand

6.3.5 Effect of ionic strength on metal ions removal

Studies on influence of electrolytes such as Ca(NO$_3$)$_2$ and NaNO$_3$ on quantitative removal of metal ions show that presence of sodium does not exhibit any significant effect on removal of Eu$^{3+}$ ions whereas slightly enhances removal of Cu$^{2+}$ and Co$^{2+}$ ions (Fig. 6.10 a). In presence of divalent cations (Ca$^{2+}$), the percentage removal of Cu$^{2+}$ and Co$^{2+}$ ions were enhanced upto a concentration of 0.1 M and then levelled off (Fig.6.10 (b)). The enhancement in percentage removal of these metal ions is due to the coagulation of suspended particles caused by divalent calcium cation which improves solid-liquid separation. In case of Eu$^{3+}$, the percentage removal increased initially upto 0.1M and then decreased gradually. This decrease in percentage removal of Eu$^{3+}$ could be explained by considering the competing interaction of Ca$^{2+}$ ions with amine, amide and xanthate functional groups of XFPD ligand.
Fig. 6.10 Effect of NaNO$_3$ and Ca(NO$_3$)$_2$ concentration on removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ ions

6.3.6 TCLP and SDLT test

Experimental results on toxicity characteristics leaching procedure (TCLP) showed 13.31%, 6.72% and 23.4% leaching of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions respectively from their complexes within 18 h. Hence, these complexes could be classified as a leaching-toxic hazardous waste and it requires additional treatment before dump into sanitary landfills.

The percentage release of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ from their respective complexes during SDLT test is given in table 6.1. The result shows that the release of metal ions at pH 3.0 is greater than at pH 7 & 11. It is also observed that percentage of leaching in first seven days is rapid and later, the rate of leaching is low. The initial rapid release of metal ions during TCLP and SDLT (at pH 3) tests is due to leaching of metal ions coordinated to nitrogen and amide group of XFPD and the subsequent slow leaching may be due to slow decomposition of metal-xanthate coordination.
6.3.7 Removal of metal ions from liquid wastes

The percentage removal of various metal ions from SNLW by xanthate process is shown in Fig.6.11 (a). It is observed that except cesium, all other metal ions are effectively removed. The percentage removal of lanthanides (Ce, Gd, La, Nd, Sm) and actinides (Th & U) are observed to > 99 %. The percentage removal of Co, Ni and Zn are observed to be greater than 90 %. The precipitation of lanthanides and transition metal ions are mainly due to metal-xanthate complex formation whereas the precipitation of actinides is due to their hydroxide formation. Hydroxides of uranium and thorium were produced due to the increase in pH of the solution during the addition of XFPD. Though alkaline earth metal ions (Ba & Sr) does not form any precipitate with XFPD ligand, their percentage removal is observed to be about 50-70 %. The removal of Ba & Sr metal ions could be explained by considering their role as coagulating agent.

On the basis of above study, experiments were performed for decontamination of radionuclides from RLW using XFPD ligand. It is observed that XFPD ligand effectively removes all radionuclides except cesium. The percentage decontamination determined for various radionuclides (Fig. 6.11 b) is in the following order:

\[ Zr \approx Eu \approx Co (>99.8) > Ce (98.84) > Sb (83.31) > Ru (79.44) > Mn (54.29) > Cs (24.02). \]
6.4. Conclusion

- A new xanthate functionalized PAMAM dendrimer (XFPD) chelating ligand, first of its kind, has been synthesized from first generation hydroxyl terminated poly(amido)amine dendrimer.

- Removal of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions from aqueous solution as a function of pH was studied. XFPD forms water insoluble complexes with Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions. The pH of the solution plays an important role on both complexation and settling of suspended metal-xanthate complex.

- Removal of metal ions was observed to be effective in the pH range of 4-8 and quick settling of suspended metal-xanthate complexes from aqueous solution at pH > 6 was achieved by the addition of aluminium sulphate. Studies on settling behavior of precipitate reveal that 3 h was sufficient for effective solid-liquid separation. The solid–liquid separation was enhanced in the presence of alkali and alkaline earth metal ions by coagulation process.

- The loading capacities of Cu$^{2+}$, Co$^{2+}$ and Eu$^{3+}$ metal ions on XFPD were estimated to be 0.48 g, 0.355 g and 0.95 g respectively per gram of XFPD at pH 4.5. The high
loading capacity of XFPD ligand is due to the presence of large number of complexing groups.

- Experiments with SNLW showed that XFPD ligand forms water insoluble complexes with various metal ions. The indigenously developed XFPD chelating ligand was deployed for the treatment of RLW and percentage decontamination of radionuclides were 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). Decontamination studies reveal that, XFPD chelating ligand is very effective for the removal of various radionuclides (except cesium) from RLW.

- The leaching of metal ions from the metal-complexes was observed and thus further studies need to be carried out for safe disposal of these complexes.