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Xanthate functionalized PAMAM dendrimer (XFPD) chelating ligand for treatment of radioactive liquid wastes

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ABSTRACT

Xanthate functionalized PAMAM dendrimer (XFPD) chelating ligand, first of its kind, has been synthesized from hydroxyl terminated poly(amido)amine dendrimer. Studies on performance of XFPD in removal of Cu^{2+} and Eu^{3+} metal ions were carried out from aqueous solution. Investigation on quantitative removal of Cu^{2+} and Eu^{3+} metal ions at various pH revealed that XFPD effectively precipitates the metal ions at pH > 4 with settling time of about 3 h. In case of Cu–XFPD complex at pH > 6, settling requires the addition of coagulating agent like aluminium sulphate. The loading capacity of XFPD for Cu^{2+} and Eu^{3+} metal ions was estimated to be 0.48 and 0.95 $g\,g^{-1}$, respectively. The XFPD chelating ligand deployed for treatment of radioactive liquid waste (RLW) showed that percentage removal of radionuclides were in the following order; $^{95}Zr \approx {}^{154}Eu \approx {}^{60}Co$ (>99.8) > ^{144}Ce (98.8) > ^{125}Sb (83.3) > ^{106}Ru (79.4) > ^{55}Mn (54.3) > ^{137}Cs (24.0). It has been demonstrated that XFPD chelating ligand has potential application in effective removal of various radionuclides from aqueous waste.

Introduction

Removal of radionuclides from aqueous waste has received renewed interest due to concern over human health and environmental hazards. Radioactive wastes in general are being generated in various processes such as mining and milling of ore, nuclear fuel fabrication, reprocessing of nuclear spent fuel and use of radioactive materials for research, medicine and industrial applications. Based on their radioactivity, the wastes are classified into three categories (i) low level waste (LLW), (ii) intermediate level waste (ILW) and (iii) high level waste (HLW) [1]. Storage of large volume of radioactive waste generated in nuclear plants and by other means is more risky and expensive [2]. Hence, these waste streams has to be treated for reducing their activity to a level at which they are permitted to be discharged as per national regulations. HLW are managed by using vitrification process following safe disposal in deep geological repository [3]. The strategy for management of LLW and ILW involves development of innovative processes with volume reduction as one of the important criteria. In general, treatment involves several processes such as filtration, precipitation, sorption, ion exchange, steam/solar evaporation and membrane separation [4]. Among these, precipitation is best suited for treatment of large volume of liquid waste containing relatively low concentration of radioactive elements. In this process both radioactive and non-radioactive metal ions are removed by using various precipitants such as hydroxides, carbonates, peroxides, sulfides, sulphates, phosphates, copper/nickel ferrocyanides etc. [5,6]. These precipitants are effective in removal of radionuclides at pH $\geq$ 8.

Organic xanthate ($R\text{-}OCS_2^-$) chelating agents form stable water insoluble complexes with various metal ions at pH > 3 [7,8]. 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 [9]. Removal of metal ions such as copper, nickel, cobalt, iron, platinum, palladium, chromium, zinc, arsenic, mercury, antimony, bismuth and lead from waste water have been already reported [10–20]. There are many advantages of using xanthate for waste treatment which includes (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 [8]. Also, metal xanthates are extensively used as fungicides, pesticides, catalyst, corrosion inhibitors, and agricultural reagents [21,22].

Organic molecules with single and multiple xanthate groups are widely studied for removal of heavy metal ions. Molecules with

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multiple xanthate group exhibit excellent binding characteristics and better settling performance [7,23]. Hence, it is desirable to increase the number of xanthate functional groups in a molecule to enhance binding and precipitating abilities. Recently, xanthate functional groups are introduced into macromolecules to increase its capacity and removal efficiency [24,25].

In the present work, the xanthate groups were introduced in dendrimer macromolecules. Dendrimers are a new class of polymeric materials which consists of a core, regularly branched dendron from the core and peripheral reactive functional groups [26]. PAMAM (Polyamidoamine) dendrimers as described by Tomalia et al. [27] are relatively easy to synthesize with desired number of reactive functional groups. The xanthate functionalized PAMAM dendrimer (XFPD) chelating ligands were synthesized for treatment of radioactive wastewater. Precipitation of Eu^{3+} and Cu^{2+} metal ions from aqueous solution using XFPD chelating ligand were studied. Europium and copper were used as homologue solutes for fission and corrosion activation products present in low level radioactive wastes produced in nuclear industries and different research activities. Effect of pH, ionic strength and settling behaviour of precipitate were investigated. Decontamination studies carried out with simulated nuclear liquid waste (SNLW) and radioactive liquid waste (RLW) are discussed.

Experimental

Materials and instruments

All the chemicals used were of analytical reagent grade. Ethylenediamine was purified by distillation over calcium hydride and all other chemicals were used as such without further purification. $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%) (Sigma–Aldrich), $CuCl_2 \cdot 2H_2O$ (98%) (Loba Chemie) were used for preparation of standard solution. Millipore water (resistivity 18.2 $M\Omega$ cm) was used in all experiments. The pH of solution was measured using Eco-testr pH 2 meter (Eutech make). Distillation was carried out using Equitron rotary evaporator. Whatman 542 hardened ashless filter paper was used for filtration. Metal complexes were dried using vacuum oven (SEMCO make). HACH turbidity meter with working range of 0–1000 NTU was used for measuring residual turbidity of the solution.

Analytical instrumentation

FT-IR spectra were recorded within a scanning range of 500–4000 cm^{-1} at 16 cm^{-1} resolution by mounting KBr pellet of the compound in (ABB) MB 3000 spectrometer. ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz spectrometer. Mass spectra were recorded using Voyager-DE^{TM} PRO matrix assisted laser desorption ionization-time of flight (MALDI-TOF) and Thermo DSQ-II quadruple mass spectrometers. Philip Model XL30 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) was used for in-situ chemical analysis of the metal precipitate. Jobin Yvow-Spex Fluorolog fluorimeter was used for measuring fluorescence emission spectra. VGEscalab MKII X-ray photoelectron spectrometer (XPS) was used to examine the oxidation state of copper and europium in Cu–XFPD and Eu–XFPD complexes. An Inductive coupled plasma optical emission spectrometer (ICP-OES) and Analytica, Janan NovAA300 atomic absorption spectrometer (AAS) were used for estimation of metal ion concentrations.

Synthesis and characterization of XFPD

The detailed synthesis and characterization of XPFD is given in Supplementary data. The synthesis involves three distinct steps (Fig. S1): (1) Michael addition of methyl acrylate with ethylenediamine, (2) amidation of ester terminated dendrimer ($PAMAMG_{0.5}$-COOMe) with tris(hydroxymethyl)aminomethane resulting in formation of hydroxyl terminated PAMAM dendrimers ($PAMAM-G_1OH$) and (3) reaction between hydroxyl group of $PAMAMG_1OH$ and carbon disulfide leading to formation of xanthate functionalized PAMAM dendrimer ($PAMAMG_1OCS_2Na$) chelating ligand (XFPD). The formation of $PAMAMG_{0.5}COOMe$ and $PAMAMG_1OH$ were confirmed by FT-IR, ^1H and ^{13}C NMR and mass spectroscopic studies. The presence of xanthate functional group in XFPD was confirmed by UV, FT-IR spectral studies and total number of xanthate group was estimated by acid–base titration.

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

Stock solutions of Cu^{2+} and Eu^{3+} metal ions (1 g l^{-1}) and XFPD (2.7860 mM) chelating agent were prepared. Precipitation studies were carried out individually with various concentrations of Cu^{2+} and Eu^{3+} metal ions (25, 50, 100, 250 and 500 mg l^{-1}) by adding 0.5 ml of 2.7860 mM XFPD ligand. The resultant precipitate was filtered through whatman 542 ashless filter paper and washed with water. The metal–XFPD precipitate was dried at 343 K in a vacuum oven and then characterized by using FT-IR, XPS and SEM-EDS.

Effect of pH on formation and settling of metal–XFPD complex

Effect of pH on removal of Cu^{2+} and Eu^{3+} metal ions were studied at pH between 3.0 and 9.0. Either 0.1 M HNO_3 or 0.1 M NaOH solutions were used for adjusting the pH of feed solution. The concentration of Cu^{2+} and Eu^{3+} metal ions in filtrate was determined by using ICP-OES. The metal ion removal efficiency for Cu^{2+} and Eu^{3+} metal ions in term of percentage removal (% *R*) was calculated by using Eq. (1).

$$\%R = \left(\frac{C_f - C_{fi}}{C_f}\right) \times 100 \tag{1}$$

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 both effective complexation and its settling. Suspended particles of metal–XFPD complex could be removed from aqueous solution by centrifugation or filtration or sedimentation process. Sedimentation process is generally used for solid–liquid separation which involves settling of suspended particles. The settling behaviour of XFPD complexes of Cu and Eu was studied by measuring residual turbidity of the solution as a function of time.

Effect of ionic strength on metal ion removal

Considering the coexistence of various electrolytes in nuclear waste and environmental samples, 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 0.01 to 0.5 M with constant metal ion to XFPD mole ratio.

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

The extent of binding (EOB) of metal ions (Cu^{2+} and Eu^{3+}) with XFPD was studied as a function of metal ion concentration. About 9 ml of metal ion (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 up to 25 ml in a standard flask. The solution was analysed to estimate the loaded metal ion on XFPD