Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808454

52 (2014) 438–445
January

Taylor & Francis
Taylor & Francis Group

Removal of cobalt from aqueous solution using xanthate functionalized dendrimer

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Received 18 April 2012; Accepted 20 March 2013

ABSTRACT

Removal of cobalt from aqueous solution by indigenously synthesized xanthate functionalized dendrimer (XFD) was investigated. Effect of pH and interference due to complexing agents/other cations on removal of cobalt by precipitation method was studied. Loading capacity of XFD as a function of cobalt concentration was estimated; about 0.355 g of cobalt could be loaded per gram of XFD at pH 4.5. It was observed that quantitative precipitation is effective at $pH > 3$ and the suspended particles are not settling down when the pH of feed solution is more than 6. The suspended particles settle down by the addition of coagulating agent (aluminum sulfate). The presence of Sr^{2+} or Mg^{2+} cations enhances precipitation process whereas monovalent Na^+ ion has no significant effect on cobalt removal by XFD ligand. Toxicity characteristics leaching procedure and semi-dynamic leaching test results show that Co-XFD complex is a characteristic leaching toxic and needs further treatment before dumping into the sanitary landfills.

Keywords: Cobalt; Dendrimer; Xanthate; Precipitation; Coagulating agent

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1. Introduction

Heavy metal contamination exists in aqueous waste stream of many industries such as metal plating facilities, mining operations, nuclear industry, and tanneries. Most of the heavy metals are potentially hazardous to living systems, and limits have been placed on their concentrations in potable water supplies and effluent discharges by different control agencies throughout the world [1,2]. Vast applications of cobalt in various arrays of products and processes such as alloys, batteries, catalysts, pigments, and coloring make this element as an important metal in various industries [3]. Cobalt is beneficial for human because it is a part of vitamin B12, which is an essential biomolecule for human health. Among the heavy metal pollutants, cobalt is one of the most widespread contaminants in the environment. The presence of Co (II) metal ion in the environment is of important concern due to its toxicity and health effects on human. It can cause neuron toxicological disorders

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Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012 and genotoxicity in human beings, and in chronic cases may cause cancer [4,5]. Hence, the recovery and removal of cobalt is very important from health, economical, and environmental point of view.

Current methods for the removal and recovery of heavy metals from wastewater include filtration, precipitation, sorption, ion exchange, electrochemical treatment, reverse osmosis, evaporation, and/or membrane separation to meet the end objectives of improved decontamination, waste volume reduction, safety, and overall cost effectiveness in the treatment, conditioning, and disposal. Precipitation process is the most widely used treatment process [6], which involves addition of suitable precipitants and then separation of precipitate from the treated wastewater by sedimentation or filtration. The inherent shortcomings in this method are requirement of large dose of alkali for adjusting pH and producing plenty of sludge as secondary pollution. Precipitation method reported by Silver [7] for cobalt removal involves oxidation of cobalt (II) to cobalt (III) and precipitation as cobalt (III) hydroxide at pH between 9 and 12. Presence of complexing agents such as EDTA and citric acid has been reported to interfere in the removal of metal ions even their concentrations are in millimolar range [8]. Hence, development of ligands and/or processes is under consideration in various countries.

Xanthates [$ROCS_2^-$] are formed by the reaction between an organic hydroxyl compound and carbon disulfide in the presence of strong base. Similar to the reaction between sodium sulfide and heavy metals, xanthates react with metals to form metal-xanthate complexes. Owing to the low solubility of metal-xanthate complexes, the xanthate treatment had been claimed to have high removal efficiency for heavy metals in wastewater [9]. These Xanthate ligands are known to coordinate with metals through various coordination modes such as monodentate, bidentate chelating, or bridging [10]. They can be easily prepared and their properties can be suitably modified by appropriate selection of alkyl substituent. In xanthate treatment, metal contaminants mostly form insoluble complexes which can be removed from solution by filtration. The formation of xanthate complexes of cobalt, nickel, copper, iron, platinum, palladium, chromium, zinc, arsenic, mercury, antimony, bismuth, and lead have been reported [9–18]. On comparison with other metal hydroxide precipitation method, xanthate treatment offers the following advantages: (i) higher degree of metal removal, (ii) less sensitivity to pH, (iii) less sensitivity to coexisting complexing agents, (iv) improved sludge dewatering properties, and (v) capability of selective removal of metals [19]. To enhance both coordinating and precipitating abilities, it is desirable to increase the number of xanthate groups in a precipitant.

Dendrimers possess hierarchical three-dimensional structures consisting of a multifunctional core from which successive branched repeating units radiate outward. Definite number of functionalities can be easily introduced at the periphery of dendrimers by exploiting the reactivity of multiple terminal groups. The reactive terminal end groups can be modified with desired functional group for various applications. Poly(amido)amine (PAMAM) dendrimers as described by Tomalia [20] are relatively easy to synthesize with number of reactive functional groups. We have introduced xanthate functional groups in first-generation hydroxyl terminated PAMAM dendrimer to enhance the chelating property of the ligand.

The present work mainly focus on experimental studies with xanthate functionalized dendrimer (XFD) on removal of cobalt metal ion from aqueous solution. Studies include the effect of pH, presence of complexing agent, and cations on precipitation of cobalt. The loading capacity of XFD as a function of cobalt concentration and settling behavior of these precipitates at various pH were studied. Additionally, toxicity characteristics leaching procedure (TCLP) and the semi-dynamic leaching test (SDLT) were conducted to investigate the metal leachability and stability characteristics of Co-XFD complex.

2. Experimental

2.1. Materials and methods

All 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. Eco-testr pH2 (Eutech) pH meter was used for pH adjustment. Millipore water (conductivity 0.055 μS/cm) was used in all experiments. Distillation was carried out using Equitron rotary evaporator and samples were dried using SEMCO vacuum oven. KS 4000i orbital shaker (IKA make) was used for equilibration study. Whatman 542 hardened ashless filter paper was used for filtration.

2.2. Synthesis of XFD

The detailed procedure for synthesis and characterization of first-generation hydroxyl terminated PAMAM dendrimer is reported elsewhere [21]. XFD was synthesized by treating first-generation hydroxyl terminated PAMAM dendrimer with CS_2 in the presence of aqueous NaOH (at the molar ratios of $PAMG_1OH:CS_2:NaOH = 1:12:12$) under vigorous stirring for overnight. The product was obtained as yellow solid after removing the solvent by using vacuum oven. The structure of XFD is given in Fig. 1.

2.3. Removal of cobalt from aqueous solution

Stock solutions of cobalt (II) metal ion (1 g/L) and XFD (2.7860 mM) were prepared. Precipitation studies were carried out with various concentrations (25, 50, 100, 250, and 500 mg/L) of cobalt (II) metal ion by adding 0.5 mL of 2.7860 mM XFD 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 vacuum oven. The residual cobalt concentration in the filtrate was determined by measuring absorbance at 520 nm in a UV-Visible spectrophotometer using Nitroso-R salt for evaluating cobalt removal efficiency of XFD. Characterization of cobalt xanthate dendrimer complex was carried out by using Fourier transform-infrared (FT-IR) spectroscopy and scanning electron microscope with energy dispersive spectrometer (SEM-EDS). Infrared spectrum was recorded using ABB MB 3000 FT-IR spectrometer. For FT-IR measurements, KBr pellet of the complex was prepared and mounted on the spectrometer. The spectrum was recorded between 400 and 4,000 cm^{-1} at room temperature. SEM provides secondary electron images of the surface with resolution in micrometer range, while EDS offers *in situ* chemical analysis of the bulk. Experiments were repeated with various concentration of cobalt nitrate solution.

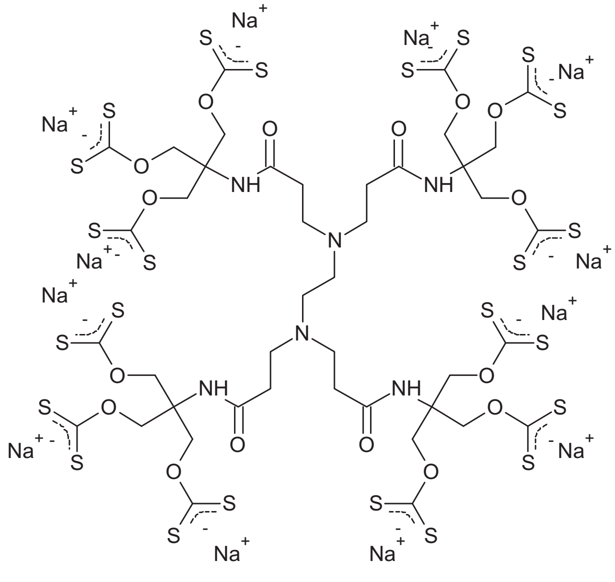


Fig. 1. Structure of XFD.

2.4. Extent of binding of cobalt

The extent of binding (EOB) of Co^{2+} as a function of metal ion concentration (between 0.85 mM and 8.5 mM) was studied with constant amount of XFD ligand. About 9 ml of Co(II) solution at pH 4.5 was taken in a 50 ml centrifuge tube and 1 ml of 2.786 mM XFD stock solution was added. The resultant precipitate was analyzed for amount of cobalt complexed with XFD. Estimation of cobalt in the precipitate involves dissolution of the precipitate in concentrated $\mathrm{HNO_3}$, evaporation to dryness, re-dissolution in water, and analysis by spectrophotometry. The filtrate was analyzed for estimation of unbound cobalt. The EOB [i.e. number of moles of cobalt complexed per mole of XFD] is expressed in Eq. (1).

$$\mathrm{EOB} = [\mathrm{Co}]_b/[\mathrm{XFD}] \tag{1}$$

where $[\mathrm{Co_b}]$ = no of moles of cobalt complexed/binded with XFD, [XFD] = no of moles of XFD in solution.

2.5. Leaching test of Co-XFD precipitate

Co-XFD precipitate was subjected to TCLP and SDLT. TCLP (USEPA, 1986) test has been recognized as a means to classify materials as hazardous or non-hazardous. SDLT provides information about stability and leaching behavior of the cobalt xanthate complex. A mixture of Co-XFD precipitate and 0.1 M acetic acid at a liquid-to-solid ratio of 20:1 was placed in a 50 ml centrifuge tube and equilibrated at 30 rpm in an orbital shaker at room temperature for 18 h. Then, the leachate was filtered through a Whatmann filter paper and the filtrate was analyzed for cobalt using spectrophotometer. In SDLT, equilibration of the precipitate was continued for 30 days with three set of leachants such as acetic acid solutions (pH 2 and 6.0) and NaOH solution (pH 11.0). During the test, the liquid-to-solid ratio was maintained as 100:1.

3. Result and discussion

3.1. FT-IR spectra

Infrared spectra of XFD and Co-XFD complex are shown in Fig. 2. In Fig. 2(a), the broad peak observed at 3,433 cm^{-1} is due to stretching vibration of –NH amide group. The bands around 1,637 and 2,924, 2,848 cm^{-1} are assigned to –C=O (–CONH) stretching and –CH stretching vibration, respectively. The peak at 1,558 cm^{-1} corresponds to –NH bending vibration of amide group. The peak at about 1,451 cm^{-1} is attributed to C–N stretching vibration.

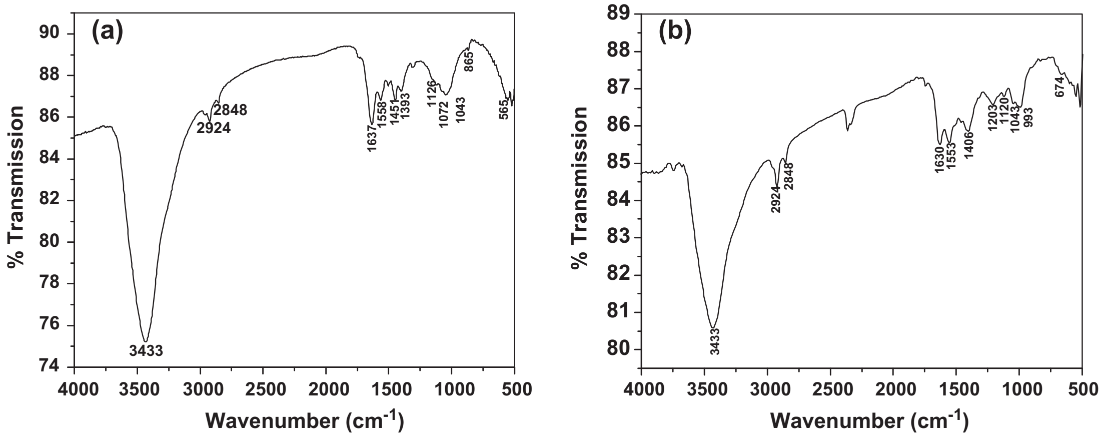
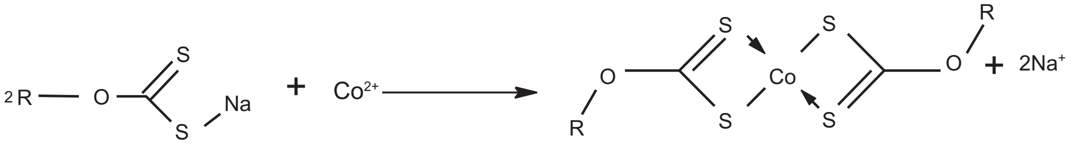


Fig. 2. FTIR spectra of XFD ligand and Co-XFD complex.

The peak at 1,393 cm^{-1} corresponds to stretching frequency of C–O–C group. The peak at 1,072 cm^{-1} is assigned to C–O stretching vibration. The presence of xanthate group in XFD gives peaks at 1,126, 1,043, and 565 cm^{-1} corresponding to stretching vibrations of S–C–S, C=S, and C–S, respectively [22]. In Fig. 2(b), the broad peak observed at 3,433 cm^{-1} is due to stretching vibration of –NH amide group. The bands around 1,630 and 2,924, 2,848 cm^{-1} are assigned to –C=O (–CONH) stretching and –CH stretching vibration, respectively. The peak at 1,553 cm^{-1} corresponds to –NH (–CONH) bending vibration. The peak at about 1,406 cm^{-1} is attributed to C–O–C stretching vibration. The peak at 1,120 cm^{-1} is assigned to C–O stretching vibration. The presence of xanthate group in Co-XFD gives peaks at 1,203, 1,049, and 674 cm^{-1} corresponding to stretching vibrations of S–C–S, C=S, and C–S, respectively. The peak at 993 cm^{-1} is the diagnostic of symmetrical coordination of the xanthate moiety [23]. The shift in vibrational frequency of S–C–S and C–S from 1,126 to 1,203 cm^{-1} and 565 to 674 cm^{-1} confirms the coordination of cobalt metal ion with xanthate group.

3.2. Formation of cobalt xanthate dendrimer complex

Formation dark-brown precipitate was observed by the addition of XFD ligand to the cobalt solution. Xanthate groups are known to coordinate with metal ions by various coordination modes such as monodentate, bidentate chelating, or bridging. In XFD ligand, along with 12 xanthate groups, nitrogen and carbonyl coordination sites are also available. Hence, more than one type of coordination is expected in the complex. Empty orbital in transition metals can be occupied by extra electrons from S, O, and N of XFD. Hence, cobalt metal ions are able to coordinate with all possible coordination sites present in the ligand. The most favorable coordination mode is bidentate chelation as shown in Eq. (2). FT-IR results confirm the formation of Co-XFD complex and SEM image (Fig. 3) shows agglomeration of particles with particle size in the range of micrometer (10 μm). The presence of cobalt metal ion in the complex was confirmed from EDS spectrum (Fig. 3).



(2)

3.3. Effect of pH on cobalt precipitation

Effect of pH on precipitation of cobalt was studied at pH ranging between 2.0 and 9.0. Exactly, 10 ml of Co^{2+} solution (50 mg/L) was taken in 50 ml centrifuge

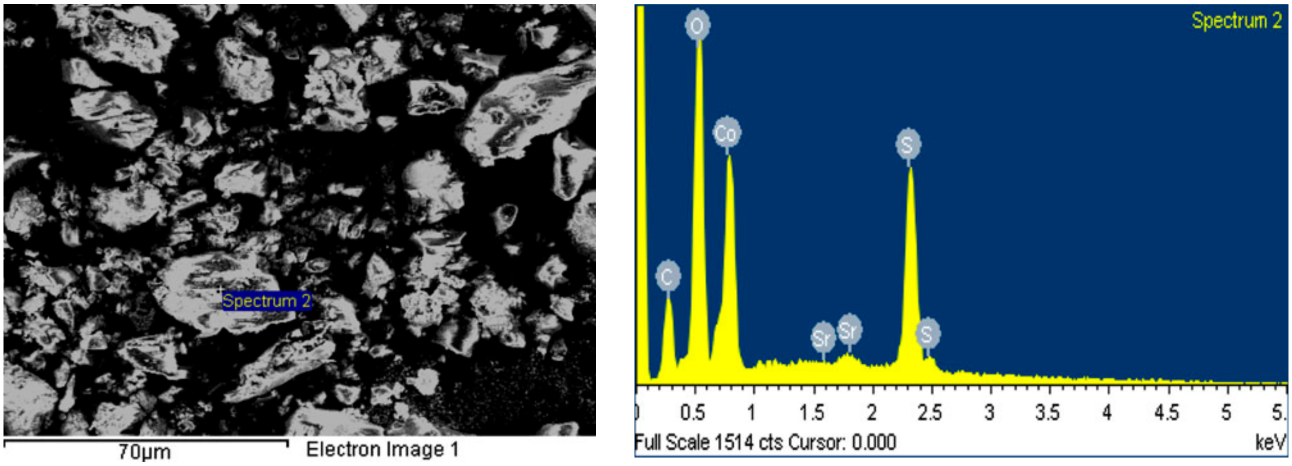


Fig. 3. SEM and EDS image of Co-XFD complex.

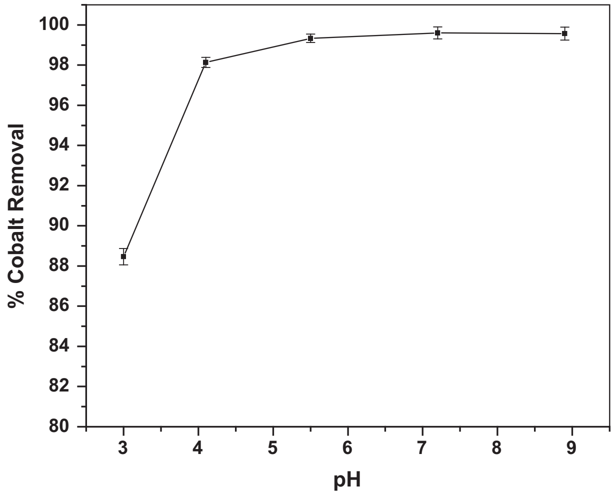


Fig. 4. Effect of pH on cobalt precipitation.

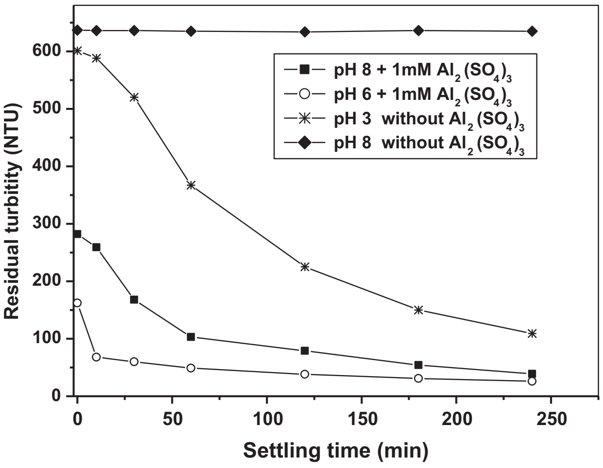


Fig. 5. Residual turbidity with settling time.

tube and pH of the solution was adjusted by adding either 0.1 M HNO_3 or NaOH. The effect of pH on uptake of Co^{2+} metal ions by XFD ligand is shown in Fig. 4. It is observed that effective precipitation (>99%) of Co-XFD complex occurs at $pH > 3$. At lower pH (<3), XFD ligand undergoes decomposition and hence, during precipitation process, pH of the feed solution should be maintained above 3. It is observed that at $pH > 6$, the suspended Co-XFD particles do not settle down and it is due to charge associated with the suspended particles. These suspended particles subsequently get coagulated into larger particles by the addition of coagulating agent (0.002 M $Al_2(SO_4)_3$). Hence, complete removal of Co-XFD complex at $pH > 6$ can be achieved by the addition of coagulating agent.

3.4. Residual turbidity with settling time

Suspended particles formed during the reaction between XFD ligand and cobalt metal ion could be removed by centrifugation or filtration or sedimentation process. Generally, a solid–liquid separation is carried out by sedimentation process which involves settling of suspended particles. Therefore, settling behavior of Co-XFD precipitate was studied by measuring the residual turbidity of the solution as a function of time (Fig. 5). It is observed that settling time of Co-XFD particles is highly dependent on pH of the solution. At pH 3.0, the precipitate possessed a favorable settling speed whereas at $pH > 6$, no settling was observed and hence requires the addition of coagulating agent ($Al_2(SO_4)_3$) for settling. After 5 minutes of agitation followed by 4 h settling, the turbidity of the solution was reduced by a factor of 5.5, 6.2, and 16.3 at pH 3.0, 6.0, and 8.0, respectively. Hence, residual turbidity can be decreased either adjusting the pH or addition of coagulating agent.

3.5. Loading capacity of XFD with cobalt

EOB for Co^{2+} as a function of metal ion concentration is shown in Fig. 6. It shows that EOB increases with increasing concentration of Co^{2+} ion and saturates at mole ratio of about 10. The high loading capacity of XFD ligand may be due to coordination of cobalt metal ion with nitrogen and carbonyl binding sites present in the XFD ligand along with 12 xanthate groups. A typical loading capacity of XFD for cobalt metal ion was measured to be 0.355 g of cobalt per gram of XFD.

3.6. Precipitation of cobalt in the presence of other complexing agent

The effect of complexing agents (citric acid and EDTA) on cobalt-XFD precipitation was studied with constant metal to ligand molar ratio of 10:1 at pH 4.5 by varying the concentration of complexing agent. The effect of complexing agent on cobalt precipitation by XFD ligand is shown in Fig. 7. The results show that citric acid does not have any significant effect on Co-XFD complex formation but affects the settling behavior of Co-XFD complex. In the presence of citric acid, settling of Co-XFD complex occurs only by the addition of $Al_2(SO_4)_3$ as coagulating agent. Presence of EDTA affects the formation of Co-XFD complex due to the formation of a strong Co-EDTA complex. The percentage removal of cobalt by XFD decreases with the addition of EDTA and a typical reduction of 50% was observed for EDTA concentration of 225 mg/L.

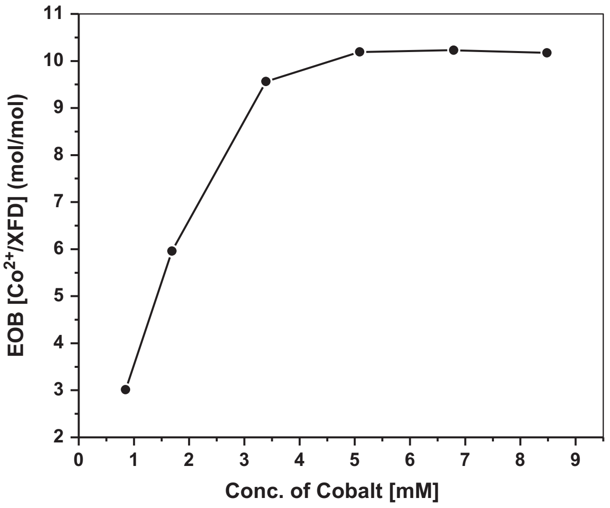


Fig. 6. EOB of cobalt with XFD.

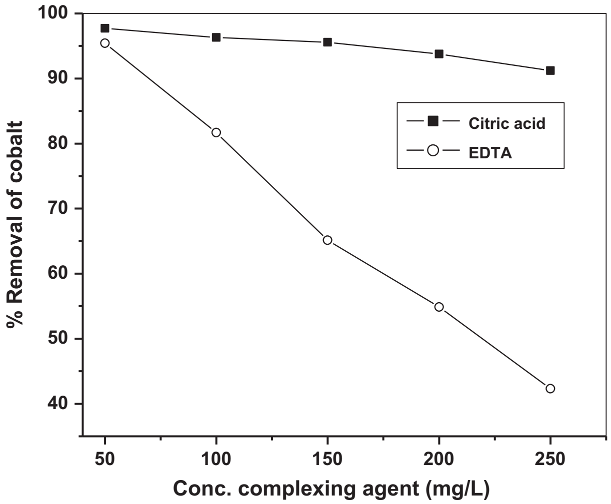


Fig. 7. Effect of complexing agent on removal of cobalt by XFD.

3.7. Effect of others cations in cobalt precipitation

The effect of metal ions such as sodium, strontium, and magnesium on cobalt precipitation was studied by carrying out experiments with various concentrations of NaCl, $Sr(NO_3)_2$ and $MgCl_2$ with constant metal ion to XFD ligand molar ratio of 10:1 at pH 4.5. The results show that the presence of sodium ion does

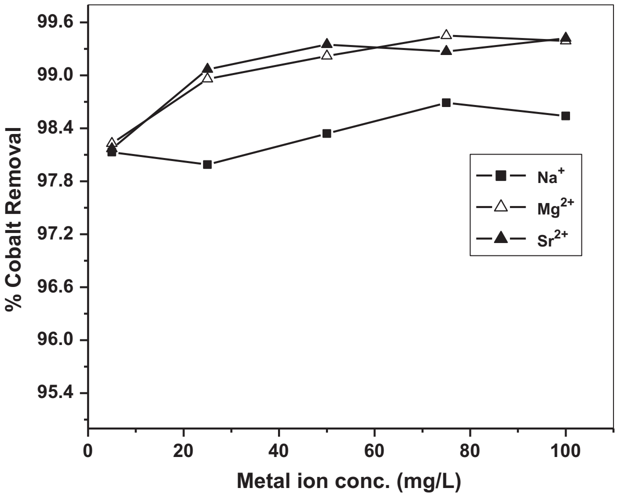


Fig. 8. Effect of cations on removal of cobalt.

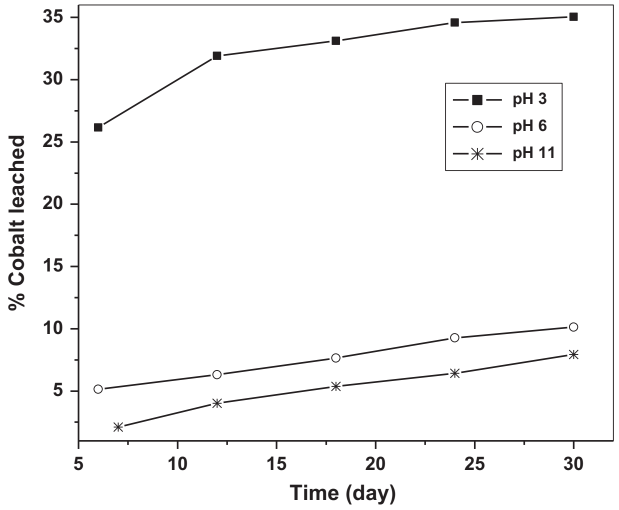


Fig. 9. Cobalt leachability at various pHs.

not have any significant effect on percentage removal of Co^{2+} ions. In the presence of divalent cations (Sr^{2+} and Mg^{2+}), the percentage removal of Co^{2+} ions increased gradually with increase in concentration of divalent cations and leveled off with further increase (>50 mg/L), as shown in Fig. 8. The enhancement in percentage removal of cobalt metal ion is due to the coagulation of suspended particles caused by divalent cations. EDS image of Co-XFD precipitate (Fig. 3) indicates the presence of strontium cation on the surface of Co-XFD complex which confirms that strontium is involved in the coagulation process.

3.8. TCLP and SDLT test

Experimental results on TCLP showed 6.72% leaching of cobalt metal ion from Co-XFD complex within 18 h. Hence, Co-XFD complex could be classified as a leaching-toxic hazardous waste and it requires additional treatment before dumping into sanitary landfills.

In addition to TCLP test, a series of SDLT using acetic acid and sodium hydroxide solution as leachant were conducted to examine the cobalt leachability and stability characteristics of the Co-XFD complex in simulated landfill environment. Samples were collected at six days interval for 30 days and concentration of cobalt in leachate was measured using Nitroso-R-salt by spectrophotometer. The release of cobalt from the Co-XFD complex during SDLT test is shown in Fig. 9. The result shows that the release of cobalt at pH 3.0 after six days is 26% and 35.04% after 30 days. It is also observed that leaching of Co^{2+} ion at the end of 30 days are 10.03% at pH 6 and 7.94% at pH 11. As it was discussed earlier, XFD ligand contains nitrogen and carbonyl coordination sites along with 12 xanthate groups. Cobalt metal ions might have coordinated with these coordination sites during precipitation process. Hence, release of cobalt metal ion during TCLP and SDLT tests is expected to be initially from nitrogen and carbonyl coordination sites followed by decomposition of cobalt–sulfur coordination.

4. Conclusion

XFD ligand forms a water insoluble complex with cobalt metal ions and can be used for removal of cobalt from waste water stream. This ligand can effectively remove cobalt at pH ranging between 3.0 and 9.0. Cobalt (II) metal ion coordinates with both anionic xanthate group and neutral nitrogen, carbonyl coordination sites. Presence of EDTA (strong complexing agent) reduces efficiency of XFD ligand. The Co-XFD complex showed favorable settling time at pH 3 and needs addition of coagulating agent at pH > 6. The high density of complexing group on XFD ligand showed higher loading capacity. Since Co-XFD complex is a characteristic leaching toxic, it needs further treatment before dump into the sanitary landfills.

Acknowledgment

The authors express their sincere gratitude to Shri S.C. Chetal, Director, IGCAR and Dr. P. Chellapandi Director, RDG for their constant encouragements. We thank Dr. K. Sivasubramanian, Head, RDS, Dr. M.T. Jose, Head, RSS, Shri H. Krishnan, Shri Shailesh joshi and Shri B.N. Mohanty RSD for their help during the experiments. We thank Dr. M. Kamuruddin, SND, MSG for SEM-EDS analysis.

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