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Performance appraisal of foam separation technology for removal of Co(II)-EDTA complexes intercalated into in-situ formed Mg-Al layered double hydroxide from radioactive liquid waste

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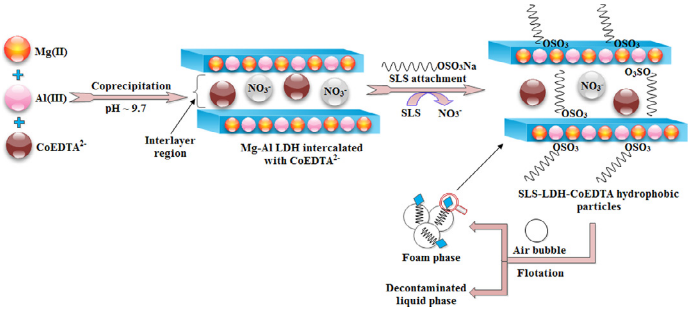
HIGHLIGHTS

- Flotation of $CoEDTA^{2-}$ intercalated into in-situ formed Mg-Al LDH was studied.
- Combination of coprecipitation/foam separation efficiently removed $CoEDTA^{2-}$ by SLS.
- High removal percentage, 99%, and high volume reduction, ~200, are obtained.
- CoEDTA-LDH was efficiently floated from radioactive liquid waste within a minute.
- The removal mechanism of $CoEDTA^{2-}$ by coprecipitation/foam separation was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Combination of coprecipitation and foam separation is suggested in this study as a new strategy for removal of $CoEDTA^{2-}$ complexes from aqueous solutions. This strategy is based on intercalation of these complexes into Mg-Al LDH colloidal particles, in-situ formed by coprecipitation process, and the subsequent separation of these particles by foam separation. The effect of the solution pH on the removal efficiency of $CoEDTA^{2-}$ is studied in the pH range of 4–12 using sodium lauryl sulfate (SLS) and cetyltrimethylammonium bromide (CTAB) as anionic and cationic collectors, respectively. The results show that SLS is better than CTAB for the present study. The influence of [Mg(II)]/[Al(III)] molar, from 0.5 to 3, showed that $CoEDTA^{2-}$ is better removed at a ratio of 2. The impact of foam separation parameters, SLS and ethanol concentrations, on removal of $CoEDTA^{2-}$ intercalated into Mg-Al LDH is evaluated. The data demonstrated that both parameters played a significant role. The effect of various competitive anions on the removal efficiency of $CoEDTA^{2-}$ is studied and their deleterious effect is followed the order $NO_3^- < Cl^- < SO_4^{2-} < CO_3^{2-}$. The efficiency of the present process is confirmed by its application for removal of $CoEDTA^{2-}$ from radioactive liquid waste where removal percentage more than 99% is achieved. The removal mechanism of the studied complex is also proposed. The efficiency of coprecipitation/foam separation process is further confirmed by comparing the data obtained for $CoEDTA^{2-}$ from radioactive liquid waste (flotation% > 99%, volume reduction = 192 and flotation time = 1 min) with those reported for removal of metal-EDTA complexes using other treatment processes.

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1. Introduction

Layered double hydroxides (LDHs), a class of anionic clays, have a general formula of $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ in which M^{2+} and M^{3+} are divalent and trivalent cations, respectively, while A is the interlayer anion with negative charge *n*. The molar ratio of $M^{3+}/(M^{2+} + M^{3+})$ gives the value of *x* which generally assumes to be between 0.20 and 0.33, and *m* is the number of interlayer water [1,2]. Due to their relatively large surface area, high anion exchange capacity, rapid production, low toxicity and a good thermal stability [3,4], LDHs have been extensively applied as anion exchangers for removal of various inorganic and organic anionic contaminants from aqueous solutions via anion exchange of the interlayer anions [3,5–7]. Since they have permanent positive charge and relatively weak interlayer bonding, LDHs are also intercalated with chelating ligands and subsequently utilized for removal of metal ions [2,8–11]. Furthermore, the interlayer regions of LDHs have been employed as intercalation hosts for anionic metal complexes [12,13]. Consequently, LDHs can be considered as promising adsorbing materials for removal of anionic metal complexes from aqueous solutions. Nevertheless, none of publications reported on LDHs have studied the removal of Co(II)-EDTA complexes from aqueous solutions. Moreover, it is reported previously that application of LDHs in the field of wastewater treatment is faced by appreciable problems in solid/liquid separation process [4]. Evaporation, decantation, centrifugation and membrane filtration are generally the conventional solid/liquid separation processes. But, the slow gravitational sedimentation rate and high energy requirement, due to dispersibility of LDH particles, make evaporation, decantation and centrifugation processes inappropriate for solid/liquid separation. Blockage of the filter, during utilization of membrane filtration, requires periodic backwashing to dispose of solids which resulted into generation of large volumes of secondary waste and eventually the filter should be replaced [14]. Thence, application of such separation processes giving rise to the increase of operation costs and time spent for the whole treatment process particularly, from the technical point of view, when large volumes of liquid wastes have to be treated. Therefore, an alternative solid-liquid separation process, namely foam separation, has been employed in the present study for removal of Co(II)-EDTA complexes intercalated into in-situ formed Mg-Al LDH particles.

The existence of ethylenediaminetetraacetic acid (EDTA), a well-known decontamination and dissolving agent at nuclear facilities, together with ^{60}Co(II) radionuclides ($t_{1/2} = 5.27$ years; high energy γ-emitter) in nuclear wastes resulted into formation of strong Co(II)-EDTA anionic complexes, mostly $CoEDTA^{2-}$, over a wide range of pH [15]. These complexes are known with their low binding with soils and sediments, which markedly increases the mobilization of radiocobalt into the environment. Besides, the conventional chemical precipitation method, which is regularly applied for treatment of radionuclide-contaminated wastewaters, is inappropriate for removal of $CoEDTA^{2-}$ complexes. According to our literature survey, few studies have been reported on the removal of EDTA-complexed cobalt from aqueous solutions. Soliman et al. [15] studied the removal of $CoEDTA^{2-}$ from aqueous solutions by ion flotation using cetylpyridinum chloride (CPyCl). At the optimum conditions, removals more than 99% are achieved within 30 min. Maximum removal percentage of about 82% is achieved for $CoEDTA^{-}$, at pH 7 and equilibration time of 12 h, by Paraneeiswaran et al. [16] via adsorption onto Pseudomonas aeruginosa SPB-1 biomass. Removal of $CoEDTA^{-}$ complex from alkaline borate solutions by nanofiltration has been studied by Sozke et al. [17] and a rejection percentage of 96% is attained at pH 11.5. Malinen and co-authors studied the sorption of radiocobalt onto titanium antiomnates in presence of EDTA [18]. The results show that removal percentage of 97% is obtained for Co^{2+}, rather than Co(II)-EDTA complex, at pH 2 and at equilibrium time of 4 days. Catalytic oxidation, using Fe-silicalites as heterogeneous Fenton-type catalyst, followed by precipitation has been applied by Sashkina et al. [19] for radiocobalt removal from EDTA chelates. Only 27% of radiocobalt is removed, as $Co(OH)_2$, by this process. From the economic and waste management points of view, these applied methods have many drawbacks (as high cost, low efficiency and time consuming) which make them inefficient for removal of EDTA-complexed radiocobalt from wastewaters. As a consequence, foam separation of Co(II)-EDTA complexes intercalated into Mg-Al LDH particles (in-situ formed by coprecipitation) is applied in this study as an alternative new strategy for removal of EDTA-complexed radiocobalt from aqueous solutions.

Foam separation is a process in which hydrophobic substances are adsorbed onto the air/liquid interface of air bubbles being introduced in the liquid phase and then removed in the foam phase a top of the solution [20]. Non-hydrophobic substances can also be removed from liquid phase by addition of a suitable surfactant, called collector, which resulted into formation of hydrophobic substances capable of attachment to air bubbles. Foam separation process is extensively applied as a solid/liquid due to its advantages, compared to the conventional processes, which include low energy consumption, low operation costs, applicability for substances of different physicochemical nature and chemical structure, flexibility of the equipment, fast operation, production of small volume of sludge and applicability for large volumes of aqueous solutions [20–22].

In the present work, combination of the conventional coprecipitation method with foam separation technology is proposed as a novel strategy for improvement the overall removal efficiency of $CoEDTA^{2-}$ complexes. This strategy involves the intercalation of $CoEDTA^{2-}$ into in-situ formed Mg-Al LDH by coprecipitation method followed by foam separation of these solid particles. Herein, the effects of various experimental conditions such as pH, [Mg(II)]/[Al(III)] molar ratio, aging time, collector and frother concentrations, EDTA concentration and the concentration of many competitive anions on the removal efficiency of LDH particles intercalated with $CoEDTA^{2-}$ has been evaluated. Furthermore, this study is extended to investigate the efficiency of the proposed method for the removal of $CoEDTA^{2-}$ from radioactive liquid waste. Afterwards, the removal mechanism of $CoEDTA^{2-}$ by combination of coprecipitation and foam separation technologies is discussed. Finally, the results obtained in the present study are compared with those reported for removal metal-EDTA complexes by using other treatment processes.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in the experimental work of this study were purchased as analytical grade purity and used directly without any further purification. Cobalt nitrate ($Co(NO_3)_2.6H_2O$) was purchased from Fluka. The radioactive ^{60}Co(II) was obtained by irradiation of cobalt nitrate in the Egypt Second Research Reactor and was used as a radiotracer during conducting the experimental work. The complexing agent ethylenediaminetetraacetic acid disodium salt ($C_{10}H_{14}N_2Na_2O_8.2H_2O$, EDTA) was purchased from Sigma-Aldrich. Magnesium nitrate ($Mg(NO_3)_2.6H_2O$, Merck) and aluminum nitrate ($Al(NO_3)_3.9H_2O$, Riedel-de Haen) were used as sources of divalent and trivalent metal cations, respectively, during the coprecipitation process for in-situ formation of Mg-Al LDH particles. The surfactants cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB) and sodium lauryl sulfate