

Sorptive flotation of Eu(III)-loaded clays from aqueous solutions

Abdelhakim Kandil¹, Amir Ezzat², Mamdoh R. Mahmoud³, Mohamed A. Soliman⁴,

Ebtissam. A. Saad²,

¹ Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt

² Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt.

³ Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority, P.O. Box 13759, Inshas, Cairo, Egypt.

⁴ Egypt Second Research Reactor, Atomic Energy Authority, P.O. Box 13759, Inshas, Cairo, Egypt.

Abstract

The present paper investigates the removal of Eu(III) from aqueous solutions by a sorptive flotation process. Eu(III) removal is achieved by adsorption onto bentonite and kaolinite followed by floatation using sodium dodecyl sulfate(SDS) and cetyltrimethylammonium bromide(CTAB) collectors. The effect of adsorption parameters (pH, contact time, clay weight, and initial Eu(III) concentration) as well as floatation parameters (collector and frother concentrations, and bubbling time) on the removal efficiency of Eu(III) were studied. Results show that Eu(III) ions are removed efficiently (~95%) at pH = 4 after 1h shaking with clays and 15min floatation

Keywords: sorptive flotation, radioactive waste, europium, bentonite, kaolinite

1.Introduction

Radioisotopes of europium (ex: ¹⁵²Eu and ¹⁵⁴Eu) are of the most hazardous contaminants present in radioactive wastewater due to their relatively high energy (hard γ -emitters) and long half-lives.[For ¹⁵²Eu($T_{1/2}$ =13.2y) three γ -lines 122,344 and 1408 keV, For ¹⁵⁴Eu($T_{1/2}$ =8.5 y) two γ -lines 123 and 1274 keV]. Besides, Eu(III) is usually taken as homologue for trivalent actinides because the ionic radii of Eu(III) is almost the same for all the trivalent lanthanides and actinides, which result in a similar physicochemical behavior of Eu(III) with the trivalent lanthanides and actinides.

Removal of radioactive contaminants is essential for environmental pollution control. Several techniques are available for the removal of hazardous ions from aqueous solutions including chemical precipitation, solvent extraction, micellar ultrafiltration, organic and inorganic ion exchangers and adsorption. Among these, the adsorption technique is considered very important because of its cost effective treatment, easy operation, narrow space for building the plant, no chemical reagents needed and no sludge produced.

Corresponding author: Abdelhakim Kandil¹ e-mail: abdelhakimkandil@yahoo.com

Natural clays are considered as a low-cost adsorbent for this purpose (Hennig et al., 2002). Various types of clays as low-cost adsorbents for heavy metal removal have been reported (Katsumata et al., 2003). Bentonite and kaolinite are well-defined naturally occurring minerals with high an adsorption capacity. The potential adsorption sites for metal ions on bentonite and kaolinite include silanol $\equiv\text{SiOH}$ and aluminol $\equiv\text{AlOH}$, hydroxyl groups on the mineral edges and the permanently charged sites $\llbracket\text{X}^-$, on the basal surface. The application of these clays for environmental pollution control in terms of metal removal from industrial effluents, leachates and contaminated ground water has received much attention (Mathews et al., 1999; Cooper et al., 2002). Hazardous metals-loaded clays are very difficult to be separated from the solution and unsuitable for column use. Researchers' attention has been focused in finding simple, less expensive and effective process for the separation of metal-loaded clays from solutions. This approach could be realized by the use of adsorptive flotation technique. This technique has shown much promise for the removal of many inorganic pollutants and radionuclides, from aqueous solutions and wastes (Cayllahua and Torem 2011; Rubio et al., 2002; Chang et al., 2009; Zamboulis et al., 2004; Santander et al., 2011).

For sorptive flotation, the ionic species to be removed (europium in the present case) is first adsorbed onto a suitable material, clay in the present case. A surfactant (the collector) is then added to the suspension and well mixed whereby it coats the surfaces of the sorbent particulates rendering them more hydrophobic. A gentle stream of fine gas bubbles is then allowed to pass through the suspension to levitate the particulates, in the form of a scum, atop the surface (Zamboulis et al., 2004)

2. Materials and Methods

Experimental

Reagents

All reagents used in this work were of analytical reagent grade chemicals and were used without further purification and all solutions were prepared with distilled water. Europium was supplied as europium (III) nitrate pentahydrate from Sigma Aldrich Company. The radioactive europium was prepared by irradiating europium nitrate in the Egypt Second Research Reactor, at Inshas site. Bentonite and kaolinite are exploited from Kasr El Sagha, Fayoum, Egypt and are commercially available.

Hydrochloric acid and ammonium hydroxide solutions, at various concentrations, prepared from the reagent grade chemicals were used to adjust the pH.

The collectors sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were obtained from Aldrich Chemical Company. Absolute ethanol was used as a frothing agent.

Sorption Experiments

The effect of pH on sorption of Eu(III) onto bentonite and kaolinite clay was carried out by contacting 10 mL of 1×10^{-4} M Eu(III) solution spiked with $^{152+154}\text{Eu}$ with 0.1 g of the sorbent in 25 mL glass bottles. The pH was carefully adjusted to the desired value by adding small amounts of dilute HCl or NH_4OH solution using a pH meter (HANNA type, HI 8519). The contact time was kept at 3h which is more than sufficient to reach equilibrium. At the end of the contact time, the samples were centrifuged for 10 min at a speed of 5,000 rpm and the remaining $^{152+154}\text{Eu}$ in the supernatant was determined.

Kinetic studies onto 0.1 g clay were carried out by batch adsorption method at temperature of 30 ± 1 °C in a temperature-controlled water bath shaker (Karl Kolb type, D-6072 Dreieich, Germany) using 25 mL Pyrex glass bottles containing 10 mL of 1×10^{-4} M Eu(III) solutions spiked with traces of $^{152+154}\text{Eu}$. The pH of the solutions was adjusted to about 4.

For all the experiments, after agitation, the solutions were centrifuged for 10 min at speed of 5,000 rpm and the remaining $^{152+154}\text{Eu}$ in the supernatant was determined radiometrically. Generally, each experiment was performed three times at least under identical conditions and the standard deviation never exceeded 4%.

For $^{152+154}\text{Eu}$ determination, the activities of solution samples before and after sorption were measured radiometrically using a well type NaI(Tl) scintillation detector connected to Ortec EG&G single channel analyzer. Removal percentage of E(III) was calculated as follows:

$$\text{Removal \%} = (A_i - A_e) / A_i \times 100 \quad (1)$$

Where A_i and A_e are the initial and equilibrium radioactivities of $^{152+154}\text{Eu}$ in the solution, respectively.

Flotation system and general procedure of sorption flotation

The flotation procedure and system used were previously described in detail (**Shakir et al., 1987; Shakir et al., 1993**). The flotation cell itself was made of G4 sintered glass disc of 3.6 cm diameter fused to a Pyrex glass column about 40 cm in height, drawn at the bottom into the form of a funnel. A tap was sealed to the flotation column at 1 cm above the sintered disc to enable sample withdrawing for analysis and pH measurement.

The flotation procedure, generally adopted, consisted of transferring 100 ml of europium-clay suspension, of the desired pH, to the flotation cell. Pure nitrogen gas was bubbled through the suspension at a rate of $25 \text{ cm}^3/\text{min}$, unless otherwise stated. The solution of the collector and ethanol was injected in one injection while vigorously stirring the suspension in the flotation cell.

3. Results and Discussion

Sorption studies

Effect of pH

The solution pH is an important factor affecting both the sorbate and sorbent properties. The effect of pH on the sorption of 1×10^{-4} M Eu(III) onto bentonite and kaolinite was carried out in the pH range of about 1–10. Fixed sorbent weight (0.1 g), constant solution volume (10 mL) and constant shaking time (1 h) were taken into consideration in studying the effect of pH. The results obtained are depicted in Fig. 1 together with the precipitation curve of Eu(III). As shown from this figure, sorption of Eu(III) onto both bentonite and kaolinite is strongly dependent on the solution pH. By increasing the solution pH, the sorption percentage Eu(III) increases to reach the maximum value at pH 4. At neutral and alkaline media, the sorption of Eu(III) ion was nearly constant due to starting of precipitation of Eu(III) as shown in the precipitation curve for europium. The reason for low sorption in acidic solution ($\text{pH} < 4$) is the competition between the excess of H^+ ions in the medium and positively charged cationic species of Eu(III) present in the solution (Parks, 1964). Also, higher acid concentrations suppress hydrolysis of the metal ions. In addition, as pH increases there is a decrease of positive surface charge, which results in lower coulombic repulsion of the sorbing metal ions (Villaescusa et al., 2000). It is observed that as the pH increases, the sorption percentage increases which can be explained on the basis of increase in the negative surface charge of clay. The variation of surface charge density with increasing pH can be a result of the ionization of surface silanol groups. With increasing adsorption density hydrogen ions pass from the surface to solution, and thus change the pH of the bulk solution (Low et al., 1995).

The negative surface charge of clay increases with increasing the pH of the medium as mentioned before. In the present study, it was supposed that there is an electrostatic attraction between the positively charged ions and the negative charged of clay.

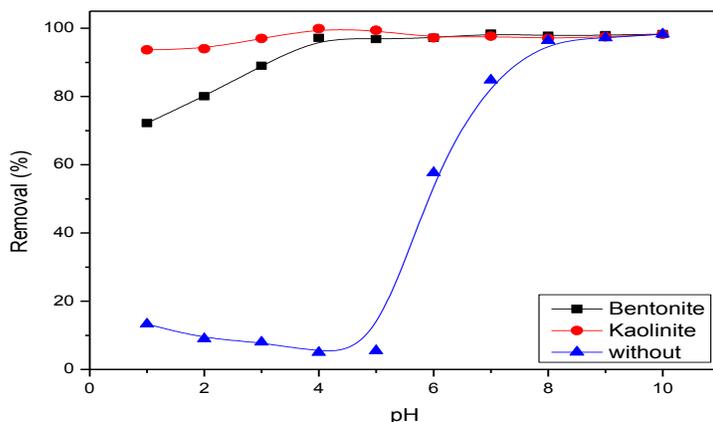


Fig. 1: Effect of the solution pH on the removal efficiency of Eu(III) by bentonite and

kaolinite. ($C_M = 10^{-4}$ M, $t_{eq} = 60$ min., clay 0.1 g, temperature 298 ± 1 K)

Kinetic studies

The effect of contact time (1 – 180 min) on sorption of 1×10^{-4} M Eu(III) onto the employed clays was investigated at pH=4 and temperature of $30 \pm 1^\circ\text{C}$ using affixed sorbent weight of 0.1g. The obtained results are shown in Fig. 2. From this figure it can be seen that the applied clays have high affinity for Eu(III) where almost complete removals are obtained for Eu(III) at 1 min. To ensure equilibration, a contact time of 60 min was applied throughout the experimental work.

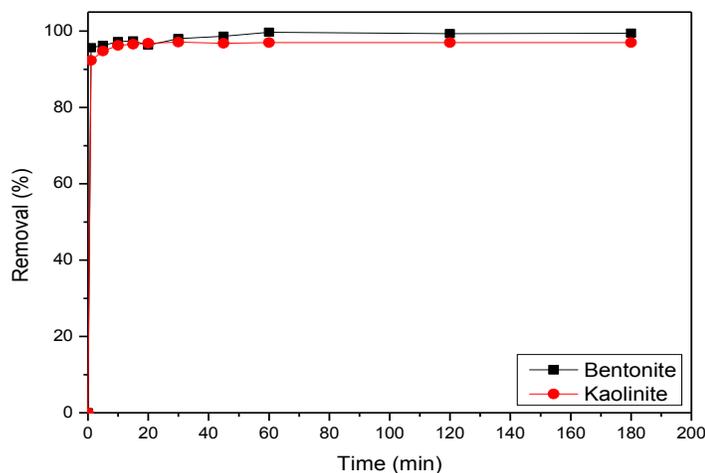


Fig. 2: Effect of contact time on adsorption of Eu(III) using bentonite and kaolinite ($C_M = 10^{-4}$ M, pH=4, clay 0.1 g, temperature 298 ± 1 K).

Effect of sorbent weight

The effect of clay weight on the sorption efficiency of 1×10^{-4} M Eu(III) is represented in Fig. 3. From this figure, it can be clearly observed that the removal efficiency of Eu(III) is slightly affected by the weight of bentonite. Removal percentages of 93.5 and $> 99\%$ are obtained at bentonite dosages of 0.01 and 0.04 g, respectively. On the other hand, the sorption process of Eu(III) is significantly dependent on the kaolinite weight. Removal percentage of 20 % is obtained at 0.01 g compared to 97.5 % at 0.1 g. At clay dosages higher than 0.04 g (for bentonite) and 0.1 g (for kaolinite), the removal percentage of Eu(III) remained unchanged. The data of this figure also indicate that Eu(III) ions are effectively removed by bentonite than kaolinite. At 0.01 g sorbent, only 20 % of Eu(III) ions are removed by kaolinite, while most of Eu(III) ions are removed ($R\% = 93.5\%$) by bentonite. Also, almost complete removals are obtained for Eu(III) ($R\% > 99\%$) using 0.04 g bentonite, while 75 % removal is obtained at the same weight using kaolinite. Increasing the removal efficiency of Eu(III) by increasing the clay weight can be attributed to the increase in the number of binding sites available for the sorption process.

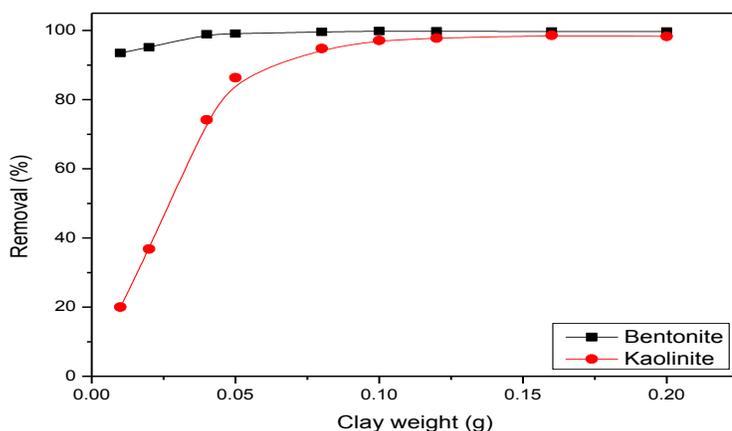


Fig. 3: Effect of adsorbent weight on the removal efficiency of Eu(III) ($C_M = 10^{-4}M$, $pH=4$, t_{eq} 60 min., temperature 298 ± 1 K).

Effect of Initial Ion Concentrations

Fig. 4 shows the effect of initial Eu(III) concentration ($1 \times 10^{-7} M - 1 \times 10^{-1} M$) on its sorption efficiency by bentonite and kaolinite. As can be seen from this figure, the applied clays had the ability to remove Eu(III) ($R\% > 99\%$) at very low concentration ($1 \times 10^{-7} M$) as well as at slightly higher concentration ($1 \times 10^{-4} M$). At Eu(III) concentrations higher than $1 \times 10^{-4} M$, the removal percentage decreased and reached 68 % (for kaolinite) and 64 % for bentonite) at 0.1 M Eu(III). The decrease in the sorption efficiency of Eu(III) with increasing its initial concentration may be due to the saturation of the adsorption sites of the clays.

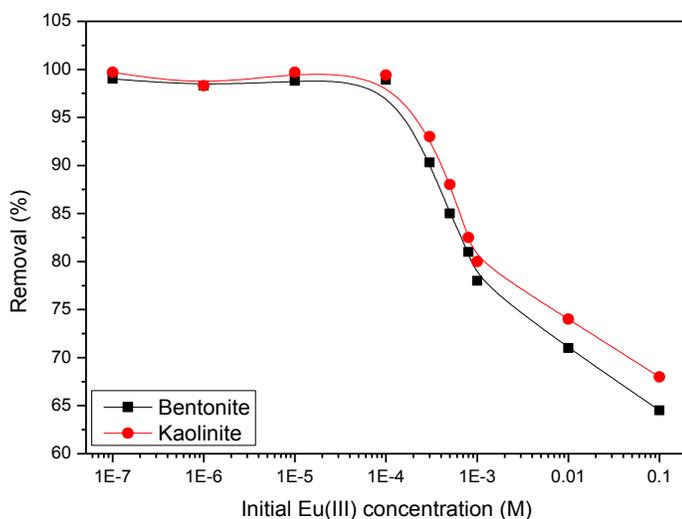


Fig. 4: Effect of initial concentration of Eu(III) on its removal percentage by the employed clays($pH=4$, t_{eq} 60 min., clay 0.1 g, temperature 298 ± 1 K)..

Sorptive flotation studies

Effect of Collector Concentration

The effect of the collector concentration on the removal efficiency of Eu(III) by ion flotation and sorptive flotation techniques is shown in Figs. 5A and 5B. From Fig. 5A, it can be noted that flotation of Eu(III) and Eu(III)-loaded clay using ion and sorptive flotation, respectively, is dependent on SDS concentration. Increasing the SDS concentration enhanced the removal percentage of Eu(III) and maximum removal of 91 % (for ion flotation and sorptive flotation of Eu-loaded kaolinite) and 96 % (for sorptive flotation of Eu-loaded bentonite) are achieved at 5×10^{-4} M SDS. At pH 4, europium presents in the aqueous as Eu^{3+} ion as indicated by the precipitation curve of Eu(III) (Fig. 1). The SDS collector ($\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$) ionized in the aqueous solutions to $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ and Na^+ . Thus, the removal percentages attained by ion flotation (Fig. 5A) can be attributed to the electrostatic attraction between the positively charged species of europium, Eu^{3+} , and the negatively charged SDS collector.

The data obtained using CTAB collector (Fig. 5B) show that insignificant removals ($R\% \sim 7\%$) are obtained for Eu(III) by ion flotation at the studied concentration range of the collector. In the aqueous solution, CTAB collector ($\text{C}_{19}\text{H}_{42}\text{NBr}$) ionized to $\text{C}_{19}\text{H}_{42}\text{N}^+$ and Br^- . Based on this, the repulsion between the positively charged europium species and CTAB cations is responsible for unfloatability of Eu(III) by ion flotation. On the contrary, Eu(III)-loaded clays are floated with CTAB and the removal efficiency of Eu(III) is increased with increasing the collector concentration and about 94 % of Eu(III) ions are removed at CTAB concentrations $\geq 5 \times 10^{-4}$ M.

Generally, Bentonite and kaolinite show polar and non-polar surface in homogeneity related to their layer structure. Adsorption of cationic CTAB surfactant occurs through electrostatic interaction between the positively charged head group of the surfactant ion and the negatively charged group of kaolinite and bentonite surface. On the other hand, adsorption of anionic SDS surfactant occurs essentially through dispersive interactions between the nonpolar hydrocarbon chain of the probe molecule and the hydrophobic mineral surface (Hezil et al., 2007).

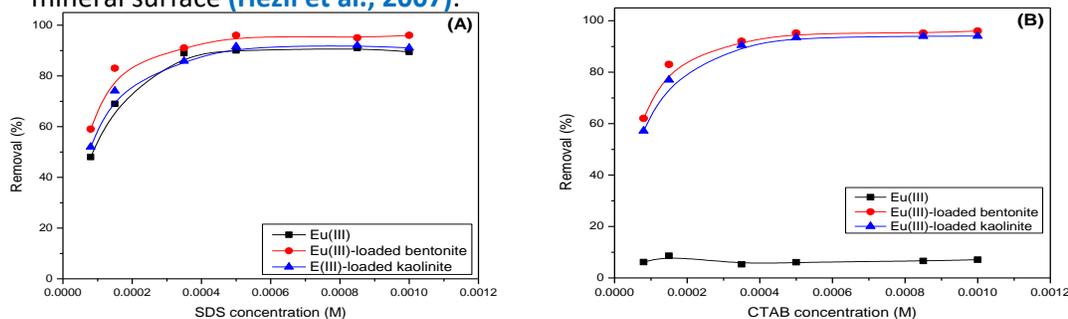


Fig. 5: Effect of collector concentration on the removal efficiency of Eu(III) by ion and sorptive flotation.

Effect of ethanol concentration

Fig. 6 illustrates the effect of ethanol concentration (0.1 – 2.5 % v/v) on the flotation of Eu(III)-loaded clays using SDS and CTAB collectors. The data given in this figure reveal that the removal percentage of Eu(III) is increased with increasing ethanol concentration and a plateau of maximum removal is achieved at 0.6 % (v/v) ethanol. At ethanol concentrations higher than 1.6 % (v/v), floatability of Eu(III)-loaded clays is deleteriously affected. Previous studies reported that the addition of a frother in flotation can simultaneously decrease the surface tension and form a stable foam layer and thus decreasing the respective bubble size via controlling bubble coalescence (Shakir et al., 2010; Cho and Laskowski, 2002; Morgan et al., 1992). Therefore, the number of bubbles available for flotation increases resulting in enhancement in the removal efficiency of Eu(III). The reduction in the flotation efficiency of Eu(III)-loaded clays at the higher studied ethanol concentrations can be attributed to the competition between ethanol molecules and the collector-colligend product (SDS- or CTAB-Eu(III)-loaded clay) for attachment with air bubbles.

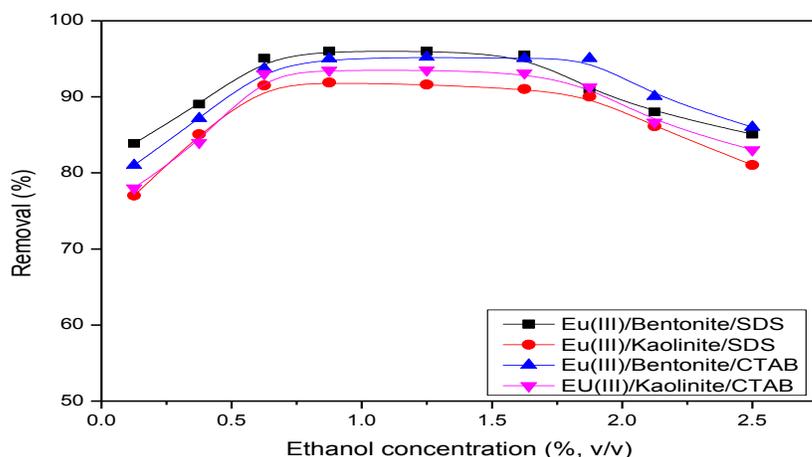


Fig. 6: Effect of ethanol concentration on the flotation efficiency of Eu(III)-loaded clays.

Effect of bubbling time

The rates of removal of the europium sorbed on clays under consideration were investigated at initial constant concentration of europium ($1 \times 10^{-4} \text{M}$), initial constant concentrations of collectors ($5 \times 10^{-4} \text{M}$), and one levels of gas flow rate. The results (Fig. 7), indicate that the kinetic curves have similar removal profiles: a relatively rapid initial rate followed by slow approach to a steady state of removal (the maximum removal or ultimate removal). Increase in bubbling time beyond the steady state of removal results in decrease in removal from the maximum due to re-dispersion of some of the dye-collector product back into the bulk solution.

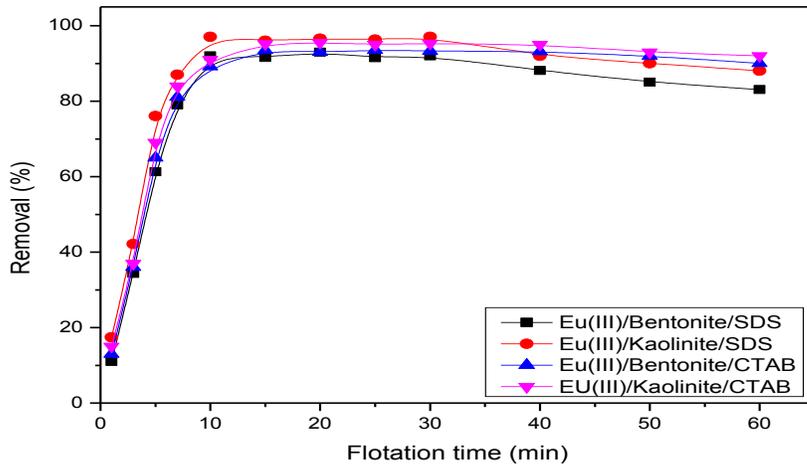


Fig. 7: Flotation of Eu(III)-loaded clays as a function in the flotation time.

4. Conclusions

Removal of Eu(III) from aqueous solutions by sorptive flotation process is studied. Eu(III) is adsorbed onto bentonite and kaolinite clays then Eu(III)-loaded clays is floated using sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) collectors. The effect of some variables as solution pH, contact time, initial sorbate concentration, and initial metal concentration on the effectiveness of employed clays for removal of $^{152-154}\text{Eu}$ from aqueous solutions were investigated. Removals > more than 99% (for bentonite) and 97% (for kaolinite) are obtained at pH= 4. Adsorption of Eu(III) onto the studied clays is a fast process and most of Eu(III) ions are removed in the first minute. At the optimum conditions (pH = 4, contact time = 60 min, clay weight = 10 g/L), the floatability of Eu(III)-loaded clay was studied at different collector and frother concentrations. Removals of (~95%) of Eu(III) are achieved using 5×10^{-4} M SDS or CTAB. Flotation of Eu(III)-loaded clays was found to directly proportional to bubbling time and reached maximum at 15 minutes.

5. References

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الملخص العربي

التعويم الامتزازي لعنصر اليوروبيوم الثلاثي المحمل على سطح الطفل من المحاليل المائية

عبد الحكيم طه قنديل^١ - أمير عزت أبو الحسن^٢ - ممدوح رفعت محمود^٣ - محمد علي سليمان^٤ - إيتسام أحمد سعد^٥

^١ قسم الكيمياء - كلية العلوم- جامعة حلوان

^٢ قسم الكيمياء- كلية العلوم- جامعة عين شمس

^٣ قسم الكيمياء النووية- المعمل الحار- هيئة الطاقة الذرية

^٤ مفاعل مصر البحثي الثاني - هيئة الطاقة الذرية

يهدف هذا البحث إلى إزالة نظير اليوروبيوم المشع من المحاليل المائية باستخدام تقنية التعويم الامتزازي. وذلك بامتزازه بواسطة الكاولين و البنتونيت وتعويم الناتج بواسطة فقاعات غازية. ولتحديد الظروف المثلى لأفضل نسبة ازالة تم دراسة بعض المتغيرات مثل الرقم الهيدروجيني ، زمن التلامس ، وكمية الطفل وكذلك تركيز ايونات عنصر اليوروبيوم . وللحصول على أفضل نسبة تعويم لليوروبيوم المحمل على الطفل تم أيضا دراسة بعض العوامل مثل تركيز المجمع ، تركيز الكحول الايثيلي وكذلك زمن التعويم. وقد أوضحت النتائج التي تم الحصول عليها أن ٩٥% تقريبا من اليوروبيوم قد تم ازالته بنجاح بالتقنية المستخدمة في هذه الدراسة.