

The Ce^{3+} Metal Ion Adsorbent Based on Calcium Alginate Loaded Fe_3O_4 (Ca-Alg/ Fe_3O_4)

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ABSTRACT

Rare earth elements frequently utilized in technological advancements is cerium. The high utilization of cerium correlates with the depletion of primary REEs reserves and the accumulation of secondary materials that can enter aquatic environments. Recycling and recovery of REEs through methods such as solvent extraction, filtration, and adsorption are commonly employed. Adsorption is chosen due to the abundance of adsorbent materials in nature, simple fabrication, efficiency, and cost-effectiveness. Calcium alginate biosorbent loaded with magnetite (Ca-Alg/ Fe_3O_4) has been used to adsorb $(Ce^{3+})_{aq}$, with optimal conditions achieved at Ca-alginate: Fe_3O_4 ratio of 2:1 (w/w), 0.075 g, pH 4, a contact time of 210 minutes, and 250 ppm, $[Ce^{3+}]_0$. The adsorption process follows the Langmuir isotherm model with q_{max} at 50.505 mg/g. Hence, the Ca-Alg/ Fe_3O_4 biosorbent shows potential in adsorbing $(Ce^{3+})_{aq}$.

INTRODUCTION

The rapid growth of industries and technology has led to an increased demand for innovative high-tech tools. Technological industrial products such as computers, electronics, telecommunications, nuclear, and aerospace industries are closely linked to rare earth elements (S. J. Suprpto, 2009). REEs play a crucial role in metallurgical materials by enhancing microstructure, alloys, refining materials, and metamorphosing inclusions (Xiong et al., 2009). Cerium is the most abundant and relatively expensive rare earth metal, applicable in various fields, some of which are highly specific. For instance, cerium oxide is suitable as a polishing agent for glass. The application of CeO₂ in polishing depends on both the physical and chemical properties, including the oxidation states of cerium, namely Ce³⁺ and Ce⁴⁺, in aqueous solutions (S. Sound et al., 2002).

Various methods have been employed for the separation and preconcentration of REEs such as precipitation, solvent extraction, ion exchange, or solid-phase extraction (Kim, 1997). Solvent extraction and ion exchange are commonly used methods; however, they are inefficient due to their requirement for large volumes and can pose health issues (Yao, 2010). These conventional methods have several drawbacks, including the use of large amounts of reagents, low selectivity, high operational costs, and the generation of secondary metabolites (Wu et al., 2004)

In recent years, research has been focused on biosorption, which has proven to be a more cost-effective method and recognized as a fast, economical, and environmentally friendly technology (Chen, 2010). One of the current candidates for sorption material is alginate. Alginate is a natural polymer with a large molecular weight, non-toxic, selective, efficient, and cost-effective. However, sodium alginate (Na-alg) is water-soluble and less stable, thus it cannot be directly used in the adsorption process. Previous research has shown the efficiency of alginate in removing various heavy metals by combining alginate with activated carbon. In recent years, magnetic particles have gained much attention due to their large surface area, high selectivity, and their ability to enhance adsorption (V. Gopalakannan & N. Viswanathan, 2015)

Several researchers have studied rare earth metal adsorption methods from solutions. For instance, Rusnadi et al. utilized the adsorbent 1-phenyl-3-methyl-4-benzoyl-5-pyrazolane (HPMBP) encapsulated in calcium alginate to adsorb Ce(III) ions in solution (Rusnadi et al., 2012). In 2007, Lim et al. conducted research on Cu(II) ion adsorption using magnetic alginate (Lim et al., 2008). Dongbei et al. developed alginate beads containing iron oxide as an adsorbent for La(III) ions (Wu et al., 2010).

In this study, the synthesis of calcium alginate containing Fe₃O₄ (Ca-Alg/Fe₃O₄) was carried out as an adsorbent for Ce³⁺ metal ions. The Ca-Alg/Fe₃O₄ was characterized using FTIR spectroscopy and SEM-EDS. Subsequently, the determination of the optimum adsorption process conditions was conducted considering various parameters such as composition, pH, adsorbent mass, contact time, along with an investigation of adsorption isotherms and the repeated use of the adsorbent.

LITERATURE REVIEW

Cerium

Cerium is one of the rare earth metals with an atomic number of 58 and an electron configuration of [Xe] 4f¹ 6s² 5d¹. Cerium finds applications in fluorescence equipment, magnetite material, and alloys. Cerium oxide is a component of catalysts used to control exhaust gases in vehicle emission control systems (Rusnadi et al., 2012)

Cerium is the most abundant rare earth metal in the Earth's crust when compared to other rare earth metals. Cerium, along with lanthanum, dominates its usage among rare earth metals, constituting approximately 80 percent in the mature market segments (such as in catalysts, glass industry, lighting, and metallurgical fields) (Goonan, 2011)

The global production of cerium metal reaches 23,000 tons per year and is expected to continue increasing due to its expanding use in everyday life (Sert et al., 2008). The increasing use of cerium may result in a higher amount of cerium ion waste being generated. This potential increase in waste poses several risks to plants, animals, and human health. The Occupational Safety and Health Administration (OSHA) sets the Permissible Exposure Limit (PEL) for cerium ions in the human body at 15 mg/m³ (Atkins. P. W, 1997). Exceeding this threshold concentration of cerium ions in the human body can lead to disruptions in various organs such as the liver, kidneys, and lungs (Murthy & Choudhary, 2011).

Alginate

Alginate" is a natural polysaccharide composed of monomers such as mannuronic acid and guluronic acid, or a combination of both. It is water-soluble, non-toxic, and easily degradable (Mortimer, 2008). Sources of alginate include brown algae such as *Laminaria hyperborean*, *Macrocystis pyrifera*, *Laminaria digitata*, *Ascophylum nodosum*, and *Lessonia nigrescens* (Mortimer, 2008). The structure of alginate consists of blocks that include G-blocks (composed of G residues), M-blocks (composed of M residues), or MG-blocks (alternating M and G residues). The structure of alginate can be observed in

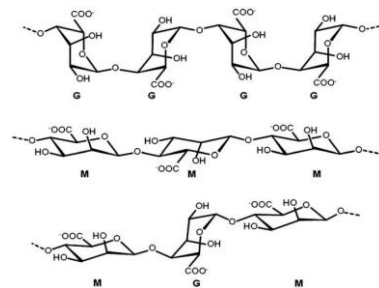


Figure 1. Alginate structure (Thanh et al., 2021)

Figure 2.1:

The structure of alginate contains multiple carboxylate groups. The presence of these negatively charged carboxylate groups enables interactions or

binding with substances or compounds that have a positive charge. This property makes alginate a commonly used adsorbent for adsorbing substances or compounds that possess a positive charge. Several studies on the use of alginate as an adsorbent have been conducted, such as the research conducted by Rusnadi, where alginate was utilized as a microcapsule adsorbent of calcium alginate containing pyrazolone ligands to adsorb rare earth metal ions (Rusnadi et al., 2012). However, using alginate as an adsorbent poses a challenge in separating the adsorbent from the solution after the adsorption process, thus requiring supporting materials to address this issue.

Magnetite or Fe₃O₄

Fe₃O₄, commonly known as magnetite, has been extensively utilized across various fields such as magnetic recording technology, pigments, and in medical treatments (Ghandoor et al., 2012). When Fe₃O₄ particles are sized between 1-10 nm, they exhibit superparamagnetic properties (Liu et al., 2002). Aside from its numerous benefits, magnetite has been employed in the purification of wastewater from metal contamination and dye substances. Fe₃O₄, being a magnetically active material, can be employed as a support material within adsorbents, simplifying the separation process of the adsorbent from the solution after the adsorption process (Panneerselvam et al., 2011).

Adsorption

Adsorption is a process where a fluid (either liquid or gas) adheres to a solid surface and forms a thin layer on that surface. It is a simple, inexpensive, and easily conducted method used to remove metal waste or dyes from water bodies (Asip & Mardhiah, 2008).

In general, adsorption is categorized into two types: physical adsorption and chemical adsorption. Physical adsorption occurs due to van der Waals forces, leading to gas condensation to form a liquid on the adsorbent surface. On the other hand, chemical adsorption happens because of a chemical reaction between the absorbed substance and the adsorbent. The amount of substance adsorbed depends on the specific properties of the solid substance and is a function of pressure and temperature. Factors influencing the adsorption capacity of the adsorbent include pH, temperature, porosity, polarity, and contact time (Asip & Mardhiah, 2008).

METHODOLOGY

Tools and Materials

The equipment used in this research includes common glassware, stoppered Erlenmeyer flasks, pestle and mortar, magnetic stirrer, analytical balance (OHAUS), shaker (OVAN OMIOE), incubator shaker, pH meter (Mettler Toledo Seven Compact), UV-Vis Spectrophotometer (Agilent 8453), Fourier Transform Infrared (FTIR) Spectrometer (Shimadzu IR Prestige-21) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) (JEOL JSM-6510A). The materials used include sodium alginate (Sigma Aldrich), FeSO₄·7H₂O (Merck), FeCl₃·6H₂O (Merck), NH₄OH (Merck), nitrogen gas, NaOH (Merck), HNO₃ (Merck), HCl 37% (Merck), CeCl₃·7H₂O (Merck),

glacial acetic acid (Merck), CH_3COONa (Merck), arsenazo III (Merck), and deionized water (aqua dm).

Synthesis of Calcium-Alginate Loaded Fe_3O_4 (Ca-Alg/ Fe_3O_4)

In this stage, the synthesis of Fe_3O_4 begins by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a 1:2 molar ratio of Fe^{2+} to Fe^{3+} into 50 mL of deionized water (aqua dm) and stirred for 60 minutes. Then, 0.1 M NH_4OH is added dropwise while continuously flowing nitrogen gas, and stirred for another 60 minutes at 60°C . The successful synthesis of Fe_3O_4 is indicated by the appearance of a black precipitate in the solution. The black precipitate is then separated using a magnetic rod and washed with deionized water until reaching a neutral pH. Afterward, the black precipitate is dried. Provide clear and concise versions of your methods of conducting research, population and samples, and data analysis tools.

The next step involves the synthesis of calcium alginate containing Fe_3O_4 . The synthesized Fe_3O_4 is added to a 2% (w/v) alginate solution and stirred for 60 minutes. Then, this mixture is gradually added drop by drop into a 2% (w/v) CaCl_2 solution, resulting in the formation of black granules. These black granules are left overnight, then washed with deionized water until reaching a neutral pH, and dried using an oven at 60°C . Ca-Alg/ Fe_3O_4 has been successfully synthesized.

Characterization of Ca-Alg/ Fe_3O_4 Adsorbent

The characterization involves Fourier Transform Infrared Spectroscopy (FTIR) to identify the functional groups present on the adsorbent before and after being used for the adsorption process. Pellets that have been prepared are measured in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. Additionally, Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) is used to examine the surface morphology of the adsorbent and the elemental composition present within the adsorbent before and after the adsorption process. Analysis is conducted at magnifications of 5000x and 10000x using a voltage of 10 kV.

Measurement of Ce^{3+} Ion Using the Arsenazo-III Method

A calibration curve for standard Ce(III) ion solutions is prepared within the concentration range of 1 ppm to 3 ppm. The calibration curve is constructed by adding a specific amount of Ce(III) solution to 0.65 mL of 0.05% arsenazo III solution and 1 mL of acetate buffer solution at pH 3.7. The solution volume is then brought up to 10 mL using deionized water (aqua dm). Absorbance measurements are taken 15 minutes after preparing the solution at a wavelength of 654 nm. The Ce(III) solution after the adsorption process is measured using the same procedure as the calibration curve, estimating the volume of Ce(III) solution taken to fall within the absorbance range of the calibration curve.

Determination of Optimum Adsorption Conditions

The determination of the optimum adsorbent composition is conducted by mixing a 1% (w/v) sodium alginate solution with varying mass compositions of Ca-Alg:Fe₃O₄, namely 4:1, 2:1, 1:1, 1:2. Subsequently, the adsorbent is exposed to 25 mL of a 100 ppm Ce³⁺ solution in a closed Erlenmeyer flask with a stirring speed of 200 rpm. The optimization involves varying the pH from 2 to 7, adsorbent mass from 0.05 to 0.175 g, contact time from 30 to 300 minutes, initial cerium concentration from 100 to 300 to study the adsorption isotherm process. Additionally, repeated testing of the adsorbent is carried out under optimal conditions determined, evaluating the Ce³⁺ ion concentration in the solution using the arsenazo III method with a UV-Vis spectrophotometer.

The adsorption capacity of Ce³⁺ ions using Ca-Alg/Fe₃O₄ adsorbent

All optimization parameters will yield data in the form of efficiency (% adsorption), capacity (q_e) adsorption generated from cerium measurements using the arsenazo III method. Some mathematical equations used are as follows:

$$\%AE = \frac{C_i - C_e}{C_i} \times 100 \dots\dots\dots(1)$$

And,

$$q_e(mg/g) = \frac{C_i - C_e}{m} \times V \dots\dots\dots(2)$$

%AE represents the adsorption efficiency (%), C_i and C_e are the initial and final concentrations of ions (mg/L), m is the mass of the adsorbent (g), and V is the volume of the solution (L). The equation used to find the Langmuir isotherm model is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \dots\dots\dots(3)$$

q_{max} indicates the maximum capacity (mg/g), and K_L represents the Langmuir constant in units of L/mg. Here is the Freundlich equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \dots\dots\dots(4)$$

The Freundlich isotherm model uses the symbol K_f for the Freundlich constant, and n represents the adsorption intensity with a value between 1 < n < 10, the adsorption process tends to be favore.

The determination of adsorption isotherms is carried out by comparing the R² values of these adsorption isotherm models. If the R² value approaches one, it indicates the closeness of the selected adsorption isotherm model to the experimental data (Dada et al., 2012).

RESEARCH RESULT

Adsorben Ca-Alg/ Fe₃O₄



Figure 2. Morphology of the adsorbent, a) wet Ca-Alg/Fe₃O₄ adsorbent, b) dried Ca-Alg/Fe₃O₄ adsorbent

Characterization of Ca-Alg/Fe₃O₄ Adsorbent Using FTIR

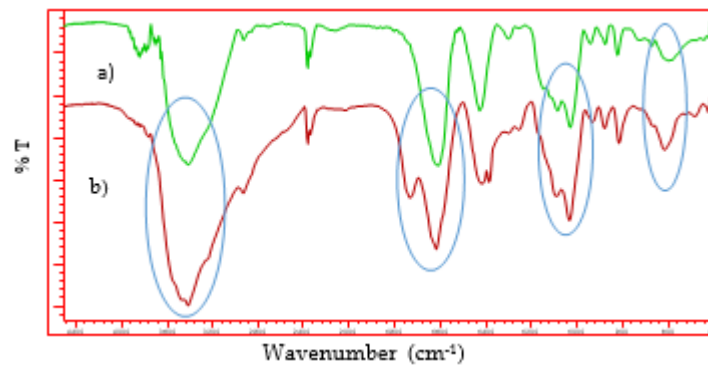


Figure 3. Spectrum of FTIR adsorbent before contact (a) and after contact (b) with Ce(III) solution

Characterization of Ca-Alg/Fe₃O₄ Adsorbent Using SEM-EDS

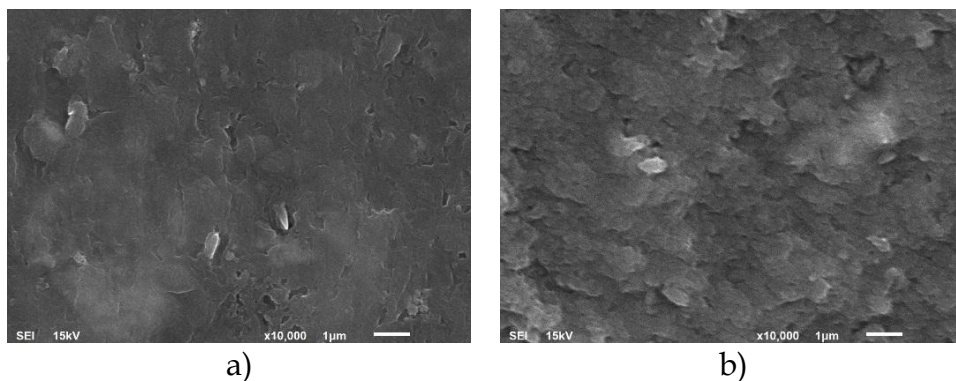


Figure 4. The SEM images of the Ca-Alg/Fe₃O₄ adsorbent, a) before being in contact with the Ce(III) solution with a magnification of 10000x and b) after being in contact with the Ce(III) solution with a magnification of 10000x.

Table 1. The results of EDS characterization of the adsorbent before and after adsorption

Elements	Percentage (%)	
	Before adsorption	After adsorption
C	39,33	44,94
O	42,67	41,04
Na	2,15	-
Cl	5,91	0,36
Ca	7,73	5,28
Fe	2,22	2,06
Ce	-	6,32

Determination of Optimum Adsorption Conditions

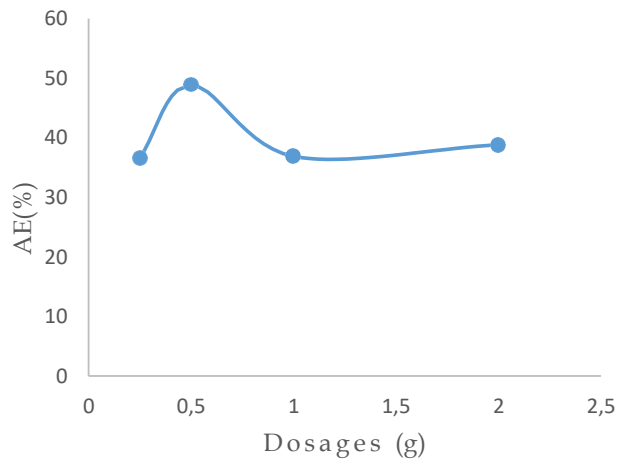


Figure 5. The effect of various adsorbent compositions on the % adsorption of Ce(III)

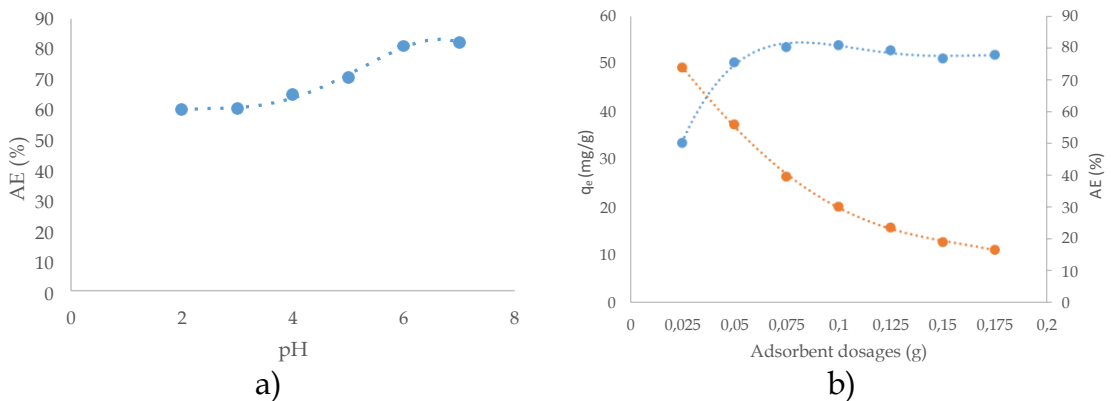


Figure 6. a) The effect of solution pH and b) adsorbent dosages on the % and capacity adsorption of Ce(III) solution

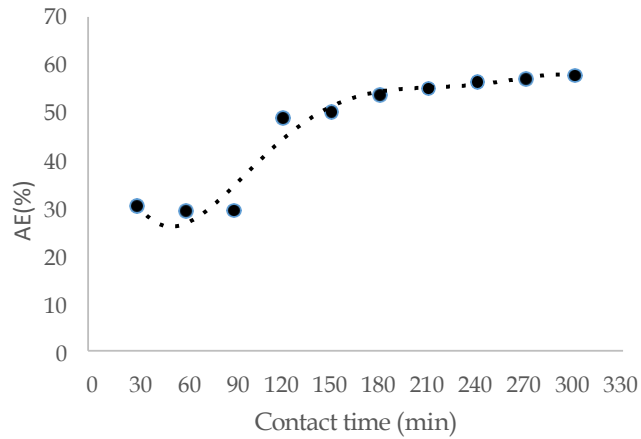


Figure 7. The effect of contact time on the % adsorption of Ce(III) solution

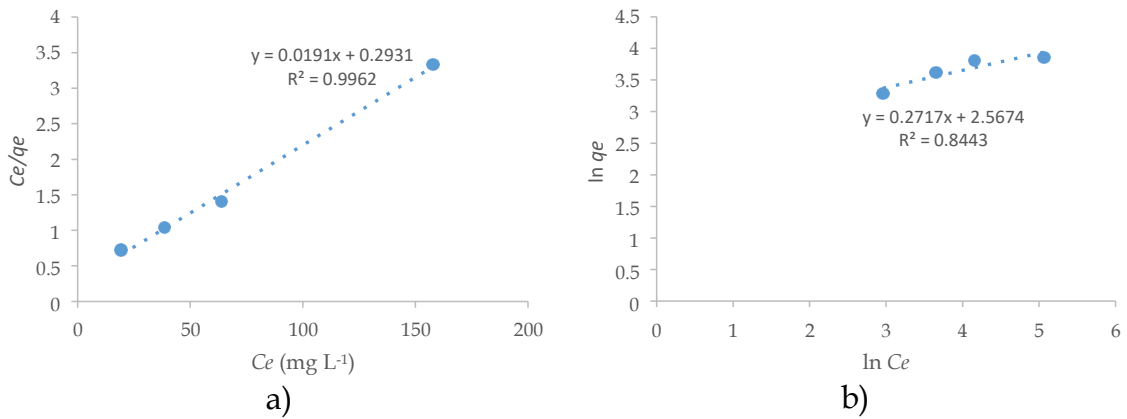


Figure 8. a) Linear form of Langmuir and b) Freundlich adsorption isotherm for Ce(III) ion adsorption

Reusability of Adsorbents

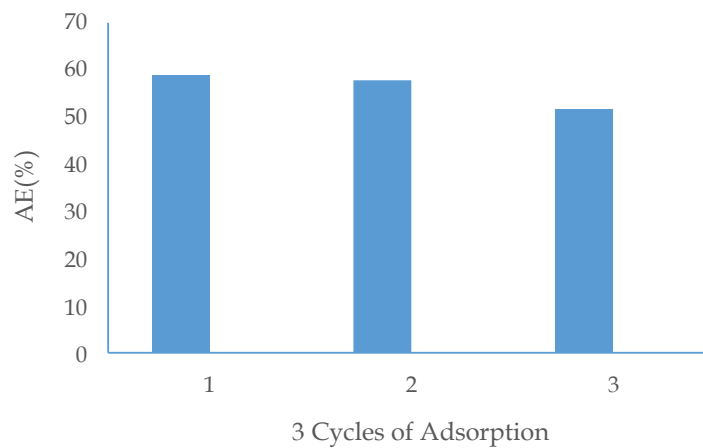


Figure 9. Reusability Cycle of Adsorbents

DISCUSSION

The adsorbent synthesis was conducted by first creating Fe_3O_4 . The formation process of Fe_3O_4 can occur in a basic environment, so ammonium hydroxide was used as a precipitating agent to minimize contamination. Sodium alginate solution mixed with Fe_3O_4 was slowly dropped into CaCl_2 to form a dark-colored gel, which was then soaked for 24 hours. Ca^{2+} ions formed cross-links with hydroxyl and carboxyl groups, resulting in calcium alginate formation. Subsequently, it was rinsed with distilled water and dried. The synthesized Ca-Alg/ Fe_3O_4 adsorbent appeared as dark-colored granules. The wet adsorbent measured 5 mm, while the dried one measured 1 mm. The physical form of the Ca-Alg/ Fe_3O_4 adsorbent is shown in Figure 2.

Figure 3, it can be observed that there is a shift in wavenumbers in the FTIR spectrum towards lower values before and after adsorption. The shift in the Fe-O group wavenumber is from 617.2 cm^{-1} to 601.7 cm^{-1} . Furthermore, the C=O group's wavenumber shifted from 1618.28 cm^{-1} to 1608.63 cm^{-1} , while the -OH group's wavenumber shifted from 3412.08 cm^{-1} to 3401.6 cm^{-1} . These wavenumber shifts occur due to the ionic interaction between the carbonyl (COO^-) and hydroxyl (-OH) groups of the adsorbent. There is an ion exchange between Ca^{2+} ions and Ce(III) ions, resulting in a change in the energy required for vibration. This indicates an interaction between the active groups of the Ca-Alg/ Fe_3O_4 adsorbent and the Ce(III) solution.

The surface morphology of the Ca-Alg/ Fe_3O_4 adsorbent in Figure 4 appears smoother before contact with the Ce(III) solution compared to the adsorbent after contact, which appears rougher. However, from these results, it cannot be definitively stated that the change in surface roughness of the adsorbent after the adsorption process is solely due to Ce(III) ions. Based on the EDS data presented in Table 1, the main composition of the Ca-Alg/ Fe_3O_4 adsorbent consists of C, O, Ca, and Fe. Meanwhile, the EDS data for the adsorbent after adsorption show the presence of cerium (Ce). Therefore, it can be inferred that the change in the adsorbent's morphology is likely due to the adsorbed Ce ions on the adsorbent surface.

The composition of the adsorbent affects its adsorption capacity for Ce(III) solution. From Figure 5, it is observed that the adsorption capability of the Ca-Alg/ Fe_3O_4 adsorbent is optimal with the addition of 0.5 g Fe_3O_4 , which occurs at a composition ratio of sodium alginate: Fe_3O_4 at 2:1 (w/w). Excessive Fe_3O_4 addition can block the pores of the calcium alginate, thereby reducing the adsorption capacity of the Ca-Alg/ Fe_3O_4 adsorbent for Ce(III) ions.

Figure 6.a demonstrates that an increase in pH contributes to an increase in the percentage of adsorption. At pH 2, the adsorption percentage of the adsorbent is very low. This is due to the high concentration of H^+ ions in the solution at low pH, resulting in competition between H^+ ions and Ce(III) ions to interact with the $-\text{COO}^-$ groups present in the alginate. As a consequence, the number of Ce(III) ions bound to the alginate decreases. The optimum pH for the adsorption process occurs at pH 4, indicated by a moderately increased % adsorption. At pH 4, the adsorbent is saturated as all active sites have bound Ce(III) ions. At pH values higher than 4, there is a concern that Ce(III) ions may

interact with OH⁻ ions, resulting in Ce(OH)₃ precipitates. Figure 6.b shows that an increase in the adsorbent mass results in a higher adsorption percentage. With a greater amount of adsorbent, there are more active sites available for the adsorption of Ce(III) ions. The % adsorption of Ce(III) ions tends to stabilize beyond an adsorbent mass of 0.075 g, suggesting that the optimal adsorbent mass for Ce(III) adsorption is 0.075 g.

An increase in contact time leads to an increase in % adsorption. The longer the contact time, the more opportunity the adsorbent has to interact with the adsorbate, resulting in a higher quantity of adsorbate being bound to the adsorbent. The optimal contact time for the adsorption process was reached at 3.5 hours. Based on figures 8.a and 8.b, it was found that the R² value for the Langmuir adsorption isotherm (R²=0.9962) is higher than the R² value for the Freundlich isotherm (R²=0.8443). This indicates that the adsorption process of Ce(III) ions by the Ca-Alg/Fe₃O₄ adsorbent follows the Langmuir isotherm model. The Langmuir isotherm model assumes that the adsorbent surface is homogeneous, and the adsorbate attached to the adsorbent surface forms a single layer (monolayer) without any interaction between adsorbates during the adsorption process.

The Ca-Alg/Fe₃O₄ adsorbent shows fairly good reusability for up to three cycles. The adsorption percentage decreases with increasing cycles, although not significantly. This indicates that the adsorbent remains effective for use up to three repeated cycles.

CONCLUSIONS AND RECOMMENDATIONS

In this study, calcium alginate adsorbent containing Fe₃O₄ (Ca-Alg/Fe₃O₄) has been successfully synthesized and found effective in adsorbing Ce(III) ions. The optimal conditions for the adsorption process were achieved at pH 4, with an adsorbent mass of 0.075 grams, and a contact time of 3.5 hours. The adsorption of Ce(III) ions using the Ca-Alg/Fe₃O₄ adsorbent follows the Langmuir adsorption isotherm model which showed a maximum adsorption capacity value of 50.505 mg/g. A regenerating agent for reusing the adsorbent is a 0.01 M HNO₃ solution. Provide some conclusions and implementation of the research results. For further research, it is necessary to conduct selectivity tests of the adsorbent using other REEs interfering ions.

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REFERENCES

- Asip, f., & mardhiah, r. (2008). *Uji efektifitas cangkang telur dalam mengadsorbsi ion fe dengan proses batch* (vol. 15, issue 2).
- Atkins. P. W, . (1997). *Kimia fisika 2*. Erlangga.
- Chen, q. (2010). Study on the adsorption of lanthanum(iii) from aqueous solution by bamboo charcoal. *Journal of rare earths*, 28, 125–131. [https://doi.org/10.1016/s1002-0721\(10\)60272-4](https://doi.org/10.1016/s1002-0721(10)60272-4)
- Dada, a. O., olalekan, a. P., olatunya, a. M., & dada, o. (2012). Langmuir, freundlich, temkin and dubinin-radushkevich isotherms studies of equilibrium sorption of zn 2+ unto phosphoric acid modified rice husk. In *iosr journal of applied chemistry (iosr-jac)* (vol. 3, issue 1). [Www.iosrjournals.org](http://www.iosrjournals.org)
- Goonan, t. G. (2011). *Rare earth elements-end use and recyclability: u.s. geological survey scientific investigations report 2011–5094*.
- Kim, j. (1997). Studies on complexation and solvent extraction of lanthanides in the presence of diaza-18-crown-6-di-isopropionic acid. *Talanta*, 45(2), 437–444. [https://doi.org/10.1016/s0039-9140\(97\)00151-3](https://doi.org/10.1016/s0039-9140(97)00151-3)
- Lim, s.-f., zheng, y.-m., zou, s.-w., & chen, j. P. (2008). Characterization of copper adsorption onto an alginate encapsulated magnetic sorbent by a combined ft-ir, xps, and mathematical modeling study. *Environmental science & technology*, 42(7), 2551–2556. <https://doi.org/10.1021/es7021889>
- Liu, z. L., liu, y. J., yao, k. L., ding, z. H., tao, j., & wang, x. (2002). Synthesis and magnetic properties of fe₃o₄ nanoparticles. *Journal of materials synthesis and processing*, 10(2), 83–87. <https://doi.org/10.1023/a:1021231527095>
- Mahmoud hamdy el ghandoor, h., zidan, h. M., khalil, m., m ismail, m. I., ghandoor, he., & khalil, m. M. (2012). Synthesis and some physical properties of magnetite (fe₃o₄) nanoparticles. In *int. J. Electrochem. Sci* (vol. 7). [Www.electrochemsci.org](http://www.electrochemsci.org)
- Mortimer, r. G. (2008). *Physical chemistry third edition*. Elsevier akademik press.
- Murthy, z. V. P., & choudhary, a. (2011). Separation of cerium from feed solution by nanofiltration. *Desalination*, 279(1–3), 428–432. <https://doi.org/10.1016/j.desal.2011.06.014>

- Panneerselvam, p., morad, n., & tan, k. A. (2011). Magnetic nanoparticle (fe₃o₄) impregnated onto tea waste for the removal of nickel(ii) from aqueous solution. *Journal of hazardous materials*, 186(1), 160–168. <https://doi.org/10.1016/j.jhazmat.2010.10.102>
- Rusnadi, r., buchari, b., amran, m. B., & wahyuningrum, d. (2012). Cerium adsorption using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (hpmbp) loaded calcium alginate beads. *Journal of engineering research and applications (ijera)*, 2, 496–862.
- S. J. Suprpto. (2009). *Tinjauan tentang unsur tanah jarang*. Bidang program dan kerja sama - pusat sumber daya geologi.
- S. Sound, m. Of, & o. U. R. Mineral. (2002). *Rare earth elements – critical resources for high technology*.
- Sert, ş., kütahyalı, c., inan, s., talip, z., çetinkaya, b., & eral, m. (2008). Biosorption of lanthanum and cerium from aqueous solutions by platanus orientalis leaf powder. *Hydrometallurgy*, 90(1), 13–18. <https://doi.org/10.1016/j.hydromet.2007.09.006>
- Thanh, t. T. T., quach, t. T. M., tran, v. T. T., nguyen, t. V., suzuki, s., kitamura, s., & yuguchi, y. (2021). Structural characteristics and biological activity of different alginate blocks extracted from brown seaweed *turbinaria ornata*. *Journal of carbohydrate chemistry*, 40(1-3), 97–114. <https://doi.org/10.1080/07328303.2021.1928155>
- V. Gopalakannan, & n. Viswanathan. (2015). Synthesis of magnetic alginate hybrid beads for efficient chromium (vi) removal. *International journal biology macromolecules*, 72, 862–867.
- Wu, d., niu, c., li, d., & bai, y. (2004). Solvent extraction of scandium(iii), yttrium(iii), lanthanum(iii) and gadolinium(iii) using cyanex 302 in heptane from hydrochloric acid solutions. *Journal of alloys and compounds*, 374(1-2), 442–446. <https://doi.org/10.1016/j.jallcom.2003.11.058>
- Wu, d., zhao, j., zhang, l., wu, q., & yang, y. (2010). Lanthanum adsorption using iron oxide loaded calcium alginate beads. *Hydrometallurgy*, 101(1-2), 76–83. <https://doi.org/10.1016/j.hydromet.2009.12.002>
- Xiong, c., meng, y., yao, c., & shen, c. (2009). Adsorption of erbium(iii) on d113-iii resin from aqueous solutions: batch and column studies. *Journal of rare earths*, 27(6), 923–931. [https://doi.org/10.1016/s1002-0721\(08\)60364-6](https://doi.org/10.1016/s1002-0721(08)60364-6)

Yao, c. (2010). Adsorption and desorption properties of d151 resin for ce(iii). *Journal of rare earths*, 28, 183–188. [https://doi.org/10.1016/s1002-0721\(10\)60324-9](https://doi.org/10.1016/s1002-0721(10)60324-9)