An effective cerium (III) ions removal method using sodium alginate-coated magnetite (Alg-Fe₃O₄) nanoparticles

Muhamad Allan Serunting, Rusnadi Rusnadi, Dian Ayu Setyorini and Bimastiyaji Surya Ramadan

ABSTRACT

In this study, the effectiveness of Ce(III) ions adsorption in aqueous solution was investigated by modifying sodium alginate with magnetite nanoparticles. The magnetite nanoparticles were coated with sodium alginate (Alg-Fe₃O₄ nanoparticles), which was prepared by the co-precipitation method. The average size of the Alg-Fe₃O₄ nanoparticles was 13.70 nm. The optimum conditions for the adsorption process were found at pH 4, 4 hours of contact time and 0.15 g of adsorbent dosage in the batch condition. The adsorption process of Ce(III) ions followed the Langmuir isotherm. The kinetic data indicated that the intraparticle diffusion process was pseudo-second order with maximum adsorption capacity (qₑ) of 31.83 mg g⁻¹. From this experiment, it can be concluded that Alg-Fe₃O₄ nanoparticles had good reusability shown by their adsorption-desorption ability using 0.01 M HNO₃ as the desorption agent.

Key words | adsorption, alginate, Ce(III), magnetite, rare earth element

INTRODUCTION

Rare earth elements (REEs) consist of 17 chemical elements including 15 lanthanides, yttrium (Y) and scandium (Sc). All these elements have been used in modern applications such as batteries in hybrid cars (NiMH batteries), phosphors for illuminated screens, fertilizers, permanent magnets used in computer hard drives and wind turbines, etc. (Sadovsky et al. 2015). Cerium is the most abundant REE in the Earth’s crust and is commonly used in fluorescent devices, polishing compounds, magnetic substances and alloys. Cerium oxide is part of the catalyst in catalytic converters that are used to clean up vehicle exhausts (Rusnadi et al. 2015). The increasing demand for cerium in human activities will lead to the possibility of environmental pollution and have negative effects for humans, animals and plants since it can be accumulated in the human body by inhalation and ingestion which can damage the kidneys and lungs (Li et al. 2015; Rim et al. 2015; Meryem et al. 2016; Zhuang et al. 2017).

Several methods have been used for metal removal from aqueous solution, such as chemical precipitation (Barboot et al. 2011), ion-exchange (Dabrowski et al. 2004), electrolysis (Petrov & Nenov 2004) and solvent extraction (Sun et al. 2016). These methods are quite expensive and difficult to operate. Recently, many researchers have begun to use the adsorption method to remove metal ions from water because this method is effective, inexpensive and easy to operate (Kushwaha et al. 2014). Alginate can be used as an adsorbent to remove metal ions from aqueous solution (Salisu et al. 2015). Alginate is a cheap material and can be found in the cell wall of brown algae which is abundant in the Indonesian seas. Alginate is a linear copolymer
consisting of (1–4) linked β-D-Mannuronic acid (M) and α-L-Guluronic acid (G) residues. The carboxylate groups of the polymer provide an ability to induce electrostatic interaction in the adsorption process (Geetha et al. 2015). When alginate is used as an adsorbent, it is difficult to separate the adsorbent from wastewater. The chemical structure of sodium alginate is presented in Figure 1.

In the last few years, researchers have published many articles related to the recovery of cerium by biomaterials adsorbent. They used brown algae (Turbinaria conoides) (Vijayaraghavan et al. 2010), agrobacterium sp. HN1 (Shuxia et al. 2011) and spirulina biomass (Sadovsky et al. 2016). Recently, magnetite nanoparticles (Fe₃O₄) have received much attention in water purification research because the materials have numerous advantages such as ease of use, simple separation from the aqueous solution and high separation efficiency (Ge et al. 2012). Zhang & Kong (2011) prepared magnetite loaded carbon nanoparticles (Fe₃O₄C) for removing organic dyes (methylene blue and cresol red) from aqueous solution. Zulfikar et al. (2015) reported that magnetite nanoparticles could be prepared by the co-precipitation method using local sands from Indonesia to adsorb humic acid. While Pandi & Viswanathan (2015) reported that magnetite nano-hydroxyapatite/alginate composite performed as a highly efficient adsorbent for defluoridation from water solution. Ge et al. (2012) also reported that magnetite nanoparticles modified with polymer (3-aminopropyltriethoxysilane and copolymer of acrylic acid and crotonic acid) could quickly remove cationic acid (crystal violet, methylene blue and alkali blue 6B) from water solution with high removal efficiency at pH 5–12. Mohammadi et al. (2014) reported that alginate coated Fe₃O₄ nanoparticles could efficiently adsorb organic dye (malachite green) from aqueous solution using the batch adsorption technique. However, only a few studies reported the adsorption of REE by this modified-alginate.
In this experiment, magnetite (Fe₃O₄) was used as the supporting material for the alginate adsorbent. There is no single report which used sodium alginate-coated magnetite (Fe₃O₄) as the adsorbent to remove cerium ions from water solution. The objective of this study was to synthesize and characterize the sodium alginate coated magnetite nanoparticles (Alg-Fe₃O₄) while the adsorption studies were carried out to optimize the conditions (pH, dosage of adsorbent, contact time, and initial concentration) of cerium adsorption using Alg-Fe₃O₄ nanoparticles in a batch method. Therefore, we want to study the isotherms and kinetics of the adsorption process.

MATERIALS AND METHODS

Reagents

All reagents were analytical grade and used directly without any further purification. The reagents were arsenazo III, CH₃COOH, and CH₃COONa purchased from Sigma Aldrich (Singapore). Sodium alginate, (NH₄)₂Fe(SO₄)₂·6H₂O, FeCl₃·6H₂O, Ce(NO₃)₃·6H₂O, NH₄OH (25%), NaOH (99%), HNO₃ (70%), HCl (25%), and H₂SO₄ (98%) were supplied by PT. Merck Tbk., Indonesia. Stock solution of Ce(III) ions 1,000 mg L⁻¹ was prepared from Ce(NO₃)₃·6H₂O salt dissolved in deionized water (DI). The adjustment of pH solution used acid solution (0.1 M HNO₃) and base solution (0.02 M NaOH). The concentration of cerium in the solutions was determined by the arsenazo III spectrophotometry method in which CH₃COOH, CH₃COONa and arsenazo III have been used as the complex compound.

Apparatus

The characterization of Alg-Fe₃O₄ nanoparticles was carried out with a UV-Vis spectrophotometer (Agilent 8453, USA) using quartz cuvette. The vibration of the functional group in the material was recorded by Fourier transform infrared (FTIR) (Shimadzu IR prestige-21, Japan), operated at 1 cm⁻¹ in the resolution range 400–4,000 cm⁻¹ region using a KBr plate. Zeta potential value was obtained by dispersing the materials in demineralized water then measuring with a Delsa™ Nano C Particle Analyzer (Beckman Coulter, USA). The structure, size and morphology of the material nanoparticles were characterized by transmission electron microscopy (TEM) (Hitachi H-7100, Japan) at 120 kV. The mapping element contained in the material was measured by energy dispersive spectroscopy (EDS) (JEOL JSM-6510A, Japan), operated at 10–20 kV. The crystal structure of the material was characterized by X-ray diffraction (XRD) (Rigaku Smartlab, Japan). The solution was agitated using a shaker (OVAN OMIOE) at 200 rpm and pH meter (Mettler Toledo Seven Compact, USA). The average size of nanoparticles was obtained from ImageJ 1.46r software.

Synthesis of Alg-Fe₃O₄ nanoparticles

Alg-Fe₃O₄ nanoparticles were synthesized using the in situ co-precipitation method following previous research by Mohammadi et al. (2014). Fe²⁺, Fe³⁺ and alginate were the precursors of this synthesis. First, 5.41 g of FeCl₃·6H₂O and 3.92 g of (NH₄)₂Fe(SO₄)₂·6H₂O (2:1 molar ratio) were dissolved in 50 mL of deionized water then 20 mL of 4% (w/v) sodium alginate aqueous solution was added and stirred for 60 minutes at room temperature. Then, ammonium hydroxide solution (30 mL of ammonium hydroxide 25% and 20 mL of deionized water) was slowly dropped into the solution. The black precipitates were separated by the magnetic field and washed several times using deionized water until neutral. Finally, Alg-Fe₃O₄ nanoparticles were dried at 60 °C for 24 hours.

Characterization of Alg-Fe₃O₄ nanoparticles

The vibration of the functional group of the adsorbent was measured by FTIR (Shimadzu IR prestige-21, Japan). The size and morphology of Alg-Fe₃O₄ nanoparticles were measured by TEM (Hitachi H-7100, Japan). The X-ray powder diffraction pattern was obtained by using XRD (Rigaku Smartlab, Japan) using Cu-Kα radiation. EDS was used for mapping elements in the sample using a JEOL JSM-6510A (Japan). Zeta potential value was measured using a Delsa™ Nano C Particle Analyzer (Beckman Coulter, USA).
Adsorption of Ce(III) ions using Alg-Fe$_3$O$_4$ nanoparticles

The variables observed for determining the optimum conditions of adsorption of Ce(III) ions were pH (pH 2–7), mass of adsorbent (0.025–0.225 g), the initial concentration of Ce(III) (25–400 mg L$^{-1}$) and contact time of adsorption (10 min–20 h). The adsorption process was conducted in batch conditions using a shaker (200 rpm) and 25 mL of volume at room temperature (25°C). After the adsorption process, the magnetic adsorbent was separated from the solution using an external magnetic field. The concentration of the solution was measured by UV-Vis spectrophotometry (arsenazo(III) method) in the wavelength of 654 nm (Sulaiman et al. 2015). The adsorption capacity of the adsorbent was determined by Equation (1):

$$\text{Adsorption capacity (}\, \text{q}_e\, \text{)} = \frac{C_i - C_e}{m} \times V$$

(1)

where $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$); $C_e$ is the concentration of ions at equilibrium (mg L$^{-1}$); $K_L$ is a constant of the Langmuir adsorption isotherm; and $q_m$ is the maximum adsorption capacity (mg g$^{-1}$).

The percentage of Ce(III) ions removal was calculated by Equation (2):

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100$$

(2)

where $C_i$ (mg L$^{-1}$) is the liquid phase initial concentration of Ce(III) ions; $C_e$ (mg L$^{-1}$) is the liquid phase concentration of Ce(III) ions at equilibrium time; $V$ (L) is the total volume of Ce(III) ions solution; and $m$ (g) is the mass of adsorbent.

Adsorption isotherm studies

Isotherm studies were conducted using seven flasks containing initial concentrations of Ce(III) ions of 25, 50, 100, 200, 250, 300 and 400 mg L$^{-1}$. The pH was kept constant at 4. Then, 0.05 g of adsorbent was added into the Ce(III) ions solution and agitated for 4 h at room temperature (25°C) until reaching equilibrium. After that, the magnetic adsorbent was separated from the solution using an external magnetic field. The adsorption capacity of the adsorbent was calculated by Equation (1). The Langmuir adsorption isotherm equation can be determined as follows (Equation (3)):

$$\frac{C_e}{q_e} = \frac{1}{K_L \, q_m} + \frac{C_e}{q_m}$$

(3)

where $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$); $C_e$ is the concentration of ions at equilibrium (mg L$^{-1}$); $K_L$ is a constant of the Langmuir adsorption isotherm; and $q_m$ is the maximum adsorption capacity (mg g$^{-1}$).

The Freundlich adsorption isotherm indicates that the adsorption is heterogeneous and categorized as multilayer adsorption. The Freundlich equation is represented as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

(4)

where $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$); $C_e$ is the concentration of ions at equilibrium (mg L$^{-1}$); $K_f$ is a constant of the Freundlich adsorption isotherm; and $n$ is the intensity of adsorption.

Adsorption kinetic studies

The adsorption kinetic was determined by agitating 100 mL of 100 mg L$^{-1}$ Ce(III) ions solution at pH 4 with 0.05 g of adsorbent for several time intervals (10, 20, 30, 60, 120, 180, 240, 300 and 1,200 min) at room temperature (25°C). The experimental adsorption kinetic data were modeled using the pseudo-first-order and pseudo-second-order kinetics. Equation (5) below shows the pseudo-first-order reaction:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} \, t$$

(5)

where $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$); $q_t$ is the adsorption capacity at a time $t$; $K_1$ is a constant of the pseudo-first-order reaction rate (min$^{-1}$); and $t$ is the contact time. $q_e$ and $K_1$ are obtained from the intercept and slope of the linear equations which connect log ($q_e - q_t$) to $t$ (Azizian 2004).

Pseudo-second-order indicates that an adsorbate is adsorbed on two active sites of the adsorbent surface (Ho & McKay 1999). The equation of pseudo-second-order is shown below (Equation (6)):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \, t$$

(6)
where $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$); $q_t$ is the adsorption capacity at a time $t$; $K_2$ is a constant of the pseudo-second-order reaction rate (g mg$^{-1}$ min$^{-1}$), and $t$ is the contact time. $q_e$ and $K_2$ are determined from the slope and intercept of the linear equations.

**Adsorption-desorption**

The desorption process was carried out using three types of acid solutions: sulfuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$) and hydrochloric acid (HCl) as the desorption agent in the concentration of 0.01 M for each solution. The desorption process was carried out by adding the adsorbent into the acid solution in various concentrations which was used first to adsorb Ce(III) ions (for the first cycle) and then stirred using a shaker at 200 rpm for 4 hours. Then the adsorbent was separated from the solution to measure the filtrate using a UV-Vis Spectrophotometer. The adsorption-desorption process was carried out in three cycles using the same adsorbent.

**Statistical analysis**

OriginPro (Version 9.0) software has been used for computational analysis. The best model was presented by the regression correlation coefficient ($r$) and standard deviation ($sd$).

**RESULTS AND DISCUSSION**

**Characterization of the Alg-Fe$_3$O$_4$ nanoparticles**

The Alg-Fe$_3$O$_4$ nanoparticles have been synthesized by the co-precipitation method in which Fe$^{2+}$, Fe$^{3+}$ and sodium alginate acted as the precursor with some modification (the source of iron salt, alginate composition for synthesis) from previous research by Mohammadi et al. (2014). The adsorbent was black powder. After the adsorption process, the adsorbent was separated by magnetic forces. This was the early evidence that the material contains magnetite (Zhang & Kong 2011).

**FTIR analysis**

The adsorbent was characterized by FTIR to observe the vibration of the functional groups on the adsorbent. The FTIR spectrum of natrium alginate, Fe$_3$O$_4$ and Alg-Fe$_3$O$_4$ nanoparticles is shown in Figure 2. The wave numbers of 489.91 cm$^{-1}$ and 570.92 cm$^{-1}$ were assigned to Fe-O in octahedral and tetrahedral sites (Zulfikar et al. 2015). Alginate also has a strong band at 1,041 cm$^{-1}$. Thus, the observed broad band at 1,043 cm$^{-1}$ is attributed to C–O–C stretching of alginate. The wave numbers 1,401.71 cm$^{-1}$ and 1,614.16 cm$^{-1}$ were the vibration of the asymmetric stretching and symmetric stretching of the carboxylate group, respectively. The broad band was obtained between 2,500 cm$^{-1}$ and 3,550 cm$^{-1}$ and attributed to the hydroxyl group (OH bond) (Rusnadi et al. 2015). According to the spectrum, it can be concluded that alginate has been successful in coating the magnetite surface.

**XRD analysis**

Figure 3 shows the diffractogram of Alg-Fe$_3$O$_4$ nanoparticles which have crystalline peaks at 2$\theta$: 30.21$\theta$, 35.57$\theta$, 43.23$\theta$, 53.69$\theta$, 57.17$\theta$ and 62.79$\theta$. The peaks on the diffractogram of the material were similar to the peaks on JCPDS card of Fe$_3$O$_4$ number 19-0629, indicating that the material synthesized contains magnetite crystals (Sobhanardakani...
The crystallite size can be calculated from the XRD pattern using the Scherrer equation:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the wavelength of incident X-ray (1.5418 Å); \( \beta \) is the width of the XRD peak at half height; \( \theta \) is the Bragg angle; and \( K \) is a shape factor having about 0.94 for magnetite and maghemite (Afkhami & Moosavi 2013). From Scherrer’s equation, the average crystallite size of alginate coated magnetite (Alg-Fe3O4) nanoparticles was 14.27 nm.

**EDS analysis**

EDS analysis presents elements in materials. It provides information regarding the differences in the percentages of the component. The percentage of elements is shown in Table 1. From Table 1, the primary elements of Alg-Fe3O4 nanoparticles are C, O and Na which come from sodium alginate; meanwhile Fe and O are derived from Fe3O4. EDS shows that there were cerium ions in the material after the adsorption process. It indicates that cerium was attached to the adsorbent surface.

**TEM analysis**

The size of Alg-Fe3O4 nanoparticles was observed by using TEM. The characterization was carried out by dispersing Alg-Fe3O4 nanoparticles powder in a solvent and then dropping onto a TEM grid. The images are shown in Figure 4. The images show that the Alg-Fe3O4 nanoparticles had a spherical shape and were about 13.7 nm in average size. The smaller the particle size of the adsorbent, the larger the surface area of the adsorbent will be (Pandi & Viswanathan 2015), thus allowing the adsorbent to react with more adsorbates. This result has the same pattern as the XRD analysis that has been explained.

**Zeta potential analysis**

Electrostatic interaction, which is usually called zeta potential, is an important factor in the adsorption process of Ce(III). It occurs because of the magnetic field on the adsorbent surface and it has been found between the adsorbent and the adsorbate Ce(III) ions. The zeta potential of Alg-Fe3O4 nanoparticles was examined by dispersing materials in demineralized water at pH 2 and 4. The results showed that the zeta potential of Alg-Fe3O4 nanoparticles at pH 2 and 4 were −5.01 and −9.46 mV, respectively. According to Zulfikar et al. (2015), the zeta potential of Fe3O4 nanoparticles in acidic solution was positive, but the coating process can change the properties of these nanoparticles. Hence, Alg-Fe3O4 nanoparticles have negative charge. The negative charge means the adsorbent Alg-Fe3O4 nanoparticles can absorb Ce(III) ions (Geetha et al. 2015; Rusnadi et al. 2015). This negative charge comes from the carboxylate group in the alginate that is coated onto the magnetite.

**The optimum conditions of adsorption of Ce(III) ions**

This section describes several optimum conditions achieved in the Ce(III) ions adsorption process by the Alg-Fe3O4 nanoparticles.
nanoparticles adsorbent. The optimum conditions of adsorption are important because they determine the best conditions for the application of the adsorbent. Some parameters including pH, contact time, adsorbent dosage and initial concentration will be described. Figure 5 shows the optimum conditions in those parameters that can be achieved by the adsorbent.

The effect of pH

The pH plays an important role in the adsorption process of Ce(III) since it affects the active group on the adsorbent surface (Aydın & Bulut 2008) and the solubility of Ce(III) ions. The influence of pH was investigated at pH of 2, 3, 4, 5, 6 and 7. Figure 5(a) shows that pH 4 was the optimum pH for the adsorption process of Ce(III) ions. Similar results were shown by Geetha et al. (2015) and Rusnadi et al. (2005) where the adsorption capacity increased by increasing pH. Since mannuronic and guluronic groups in alginate have pKa of 3.38 and 3.65, the adsorption capacity is increasing linearly with pH (Febrianto et al. 2013).

At acid conditions (e.g. pH 2), the adsorbent surface would be protonated causing positive charge of the adsorbent surface. At pH 4, those groups are deprotonated which results in the charge of the adsorbent surface becoming negative. This condition will attract Ce(III) which had positive charge and induces the electrostatic interaction in the surface (Mohammadi et al. 2014). When pH was lower than 4, the adsorbent surface was protonated which made the interaction between adsorbent and Ce(III) ions more difficult. Otherwise, when pH was higher than 4, the adsorption capacity did not actually increase. It might have increased because Ce(III) ions interacted with OH− groups and formed Ce(OH)3. Precipitation of cerium started and thus experiments were not conducted above pH 5.5 (Bouchaud et al. 2012). The excess solution after the adsorption process was measured using UV-Vis spectrophotometry and it gave a low adsorption value.

The effect of contact time

The adsorption capacity of Alg-Fe3O4 nanoparticles was investigated with different spans of contact time (range 10 minutes to 20 hours) with initial concentration of Ce(III) 100 mg L−1 and with an adsorbent dosage 0.05 g at room temperature (25 °C). Figure 5(b) shows that the adsorption capacity increased with increasing contact time until a contact time of 4 hours. The longer contact time might give a longer time for the adsorbate to interact with the adsorbent surface. When the contact time was longer than 4 hours, the adsorption capacity did not significantly increase. This was because the adsorbent surface had been covered up with Ce(III) ions so the adsorbent could not adsorb more adsorbate (Firdaus et al. 2017).

The influence of adsorbent dosage

The optimum mass parameter aims to estimate the dose required in the use of the adsorbent under several
conditions of this study. Adsorbent dosage is related to the number of active sites on the adsorbent surface. Increasing the adsorbent dosage will increase the number of active sites on the adsorbent surface. In Figure 5(c), the percentage of adsorption increased as long as the adsorbent mass increased until it reached equilibrium. The optimum adsorbent mass to adsorb 25 mL of 100 mg L\(^{-1}\) Ce(III) ions was 0.15 g. When the adsorbent dosage was more than 0.15 g, the percentage of adsorption was constant. This was because the active sites on the adsorbent surface had interacted with all of the adsorbate. So, no more adsorbate interacted with active sites (Sobhanardakani et al. 2016).

Figure 5 | Dependence of adsorption process on (a) pH of solution, (b) contact time, (c) adsorbent dosage and (d) initial concentration.

The effect of initial concentration of Ce(III) ions

The adsorption capacity also increased due to the increasing of the initial concentration of Ce(III) ions solution which can be seen in Figure 5(d). If the initial concentration of adsorbate was high, it would give a chance for Ce(III) ions to interact with the active sites on the adsorbent surface (Zulfiqar et al. 2015). The adsorption capacity increased sharply as the initial concentration increased from 25 to 200 mg L\(^{-1}\) but when the initial concentration was higher than 200 mg L\(^{-1}\), the adsorption capacity tended to be constant. Based on the experimental data, the maximum adsorption capacity (\(q_m\)) of Alg-Fe\(_3\)O\(_4\) nanoparticles to
adsorb Ce(III) ions was 31.83 mg g$^{-1}$. The higher adsorption rate in this experiment might be contributed to by functional groups such as hydroxyl and carboxylate on the Alg-Fe$_3$O$_4$ nanoparticle surface which have negative charge (Rusnadi et al. 2013). This condition indicated that there was electrostatic interaction between the adsorbent surface and the Ce(III) ions. This result shows that Alg-Fe$_3$O$_4$ nanoparticles have the potential to be an adsorbent for the recovery of cerium ions from solution.

**Adsorption isotherms**

The study of adsorption equilibrium provides information about the adsorption capacity of the adsorbent. The adsorption isotherm can be characterized by the value of a certain constant that expresses the adsorbent surface properties and affinity (Rahimi & Vadi 2014). There are two common adsorption isotherms models, the Langmuir model and Freundlich model. The adsorption isotherm is determined by comparing the $R^2$ value of the linear isotherm model (Kushwaha et al. 2014). It fits the isotherm model if $R^2$ is close to unity.

The correlation coefficients ($R^2$) of linear fitting are shown in Table 2, the Langmuir isotherm model (0.9983) is closer to unity than the Freundlich's (0.9865) so it can be concluded that the adsorption process in this study followed the Langmuir isotherm model. Figure 6 shows the fitting plot non-linear model for Langmuir and Freundlich isotherms. It reconfirms that the experiment was following the Langmuir isotherm. The Langmuir isotherm model assumes that the adsorption is homogeneous and is categorized as monolayer adsorption with a limited number of active sites. If the monolayer has been formed, no more layers are formed, then the adsorbent surface will reach a saturation point and the maximum adsorption capacity of the adsorbent surface will be achieved (Boparai et al. 2011).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The parameters of Langmuir and Freundlich isotherms</th>
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<td><strong>Freundlich</strong></td>
<td><strong>Langmuir</strong></td>
</tr>
<tr>
<td>$K_F$</td>
<td>$n$</td>
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<tr>
<td>9.2424</td>
<td>4.4248</td>
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The Freundlich isotherm constant value ($K_F$) is calculated from the slope and intercept of the equation of the $C_e$ curve line with ln $q_e$. The affinity of the interaction between adsorbent and adsorbate can be explained by the value of the adsorption intensity ($n$), the value $1 < n < 10$ illustrates that adsorption tends to be favored. Table 2 also shows $R_L$ values which are a factor of Langmuir isotherms that can be used to predict the affinity between adsorbent and adsorbate. In this research, the $R_L$ value is in the range of 0.03 to 0.35. This indicates that the adsorption process is favored. Based on the literature Al-Rub et al. (2004), if the value of $R_L > 1$ then the adsorption process is not preferred, if the value $R_L = 1$ then the adsorption process is linear, if $0 < R_L < 1$ then the adsorption process is favorable, and for $R_L = 0$ the adsorption process is irreversible (Al-Rub et al. 2004).

**Adsorption kinetic**

The mechanism of adsorption kinetic in this research was investigated with pseudo-first-order and pseudo-second-order models. Pseudo-first-order explains that the adsorption kinetic in a solid-liquid system is due to the adsorption capacity of the solid phase and it assumes that an adsorbate is adsorbed on an active site on the adsorbent surface (Azizian 2004).

The reaction follows an adsorption kinetic model if $R^2$ is close to unity. In this experiment, the adsorption kinetic was following pseudo-second-order with $R^2$ of 0.9959 otherwise.
the $R^2$ of pseudo-first-order was 0.8742, as shown in Table 3. The comparison of pseudo-first-order and pseudo-second-order for this experiment is presented in Table 3.

### Adsorption-desorption study

Reusability of an adsorbent is an important factor. It can be determined by conducting adsorption-desorption in three cycles (Sadovsky et al. 2016). Desorption of Ce(III) uses an acidic agent because $H^+$ ions can push Ce(III) ions out which are attached to the adsorbent surface. In this study, the desorption agent was varied using $HNO_3$, $HCl$ and $H_2SO_4$ in the concentration of 0.01 M for each solution. Those solutions could desorb Ce(III) ions in three cycles although the adsorption capacity decreased. This was because there were active sites (in this matter carboxylic group) which were leached when the desorption process occurred. 0.01 M $HNO_3$ showed a good result compared to $HCl$ and $H_2SO_4$. Its percentages of adsorption were 93.14, 66.54 and 61.62% for each cycle as shown in Figure 7.

This is in agreement with the result obtained by Sadovsky et al. (2016) using 0.1 mol L$^{-1}$ $HNO_3$ to investigate the efficiency of regeneration and reuse of the Spirulina biomass to adsorb Ce(III) ions (Sadovsky et al. 2016).

### Comparative studies

The adsorption capacity of Alg-Fe$_3$O$_4$ nanoparticles to adsorb Ce(III) ions was compared with other adsorbents that have been reported, in Table 4. The modified materials Alg-Fe$_3$O$_4$ nanoparticles were potentially applied to remove Ce(III) from water solution.

### Practical application and future perspectives

As REEs are used as components in high technology devices, including smart phones, digital cameras, computer hard disks, fluorescent and light-emitting-diode (LED) lights, flat screen televisions, computer monitors, and electronic displays, the potential for environmental pollution will be increasing year by year (United States Geological Survey [USGS] Mineral Resources Program 2014). This kind of adsorbent (modified alginate), can be an alternative material to remove cerium(III) from wastewater. Indonesia is a maritime country which is dominated by sea. Therefore, it has abundant brown algae. Alginate is derived from brown algae cell wall which has not been used effectively until now. Adsorbent from alginate is easy to synthesize (Pandi & Viswanathan 2014; Geetha et al. 2015). The procedure already stated in this article can be used to produce commercial adsorbent of Alg-Fe$_3$O$_4$ nanoparticles. The results showed that Alg-Fe$_3$O$_4$ nanoparticles performed well in adsorbing Ce(III) from the solution. The synthetic material is expected to be applied in daily life. The material can also be applied in mining companies because cerium (III)
pollution can be derived from the side waste of the mining process. The material is dispersed in wastewater where metal ions will be adsorbed on the surface of the material. The material can be recovered again using a magnetic rod. In this experiment, the magnetic properties of the adsorbent were not observed. For the future research development, it will be better if the magnetic properties are observed using magnetometer. The selectivity of the adsorbent also needs to be observed using other REEs.

CONCLUSION

In summary, sodium alginate-coated magnetite (Alg-Fe3O4) nanoparticles were successfully synthesized using the co-precipitation method. The average size of the Alg-Fe3O4 nanoparticles was about 13.70 nm. The optimum conditions for adsorption of Ce(III) ions were pH 4, with a contact time of 4 hours and adsorbent dosage of 0.15 g with a batch method. This adsorbent showed good performance in reusability. Its adsorption-desorption ability was about three cycles using 0.01 M HNO3 as the desorption agent. The adsorbent alginate-coated magnetite (Alg-Fe3O4) nanoparticles showed a good adsorption capacity. It has the potential to effectively contribute to removal of Ce(III) ions from solution.

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