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ADSORPTION OF LANTHANIDE IONS FROM AN AQUEOUS SOLUTION IN MULTICOMPONENT SYSTEMS USING ACTIVATED CARBON FROM BANANA PEELS (*MUSA PARADISIACA L.*)

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ABSTRACT

Lanthanides in aqueous waste streams have received great attention due to their ability to pollute the environment. Therefore, efforts have been devoted to adsorbing lanthanides from waste industries. The evaluation of agro-waste by determining the adsorption efficiency of Ln^{3+} ions is an important step in developing a process for Ln^{3+} removal from water systems, as well as a method of isolating Ln^{3+} ions from mineral ores, such as low-grade bauxite. The adsorption performance of banana peels (*Musa paradisiaca L.*) was evaluated in the removal of Ln^{3+} ions. In addition, the adsorption of lanthanide ions from an aqueous solution in a multicomponent system was studied using activated carbon from banana peels. The selection of the best adsorbent was done by the iodine number method, where activated carbon had the highest iodine absorbance at 572.2 mg/g. The use of activated carbon as an adsorbent for the removal of commercial lanthanide ions from an aqueous solution was evaluated. The optimum condition in the Ln^{3+} multicomponent system for the adsorption of Y^{3+}, La^{3+}, Ce^{3+}, Nd^{3+}, and Sm^{3+} ions was determined to be a contact time of 2.5 h, a pH of 4, and an adsorbent dosage of 100 mg. The present research further supports the possibility of the adsorption of Ln^{3+} ions from low-grade bauxite with adsorption efficiencies of 67.6, 71.0, 65.0, 62.9, and 56.6% for Y^{3+}, La^{3+}, Ce^{3+}, Nd^{3+}, and Sm^{3+}, respectively.

Keywords: Activated carbon; Adsorption; Banana peels; Lanthanides; Low-grade bauxite; Multicomponent system

1. INTRODUCTION

Lanthanides are critical materials for advanced and high technologies in many applications, particularly those in the energy, optic, electronic, chemical, automotive, defence (King et al., 2018), and nuclear power industries (Elsalamouny et al., 2017). The trivalent state of lanthanide is the most thermodynamically stable form in an aqueous solution (Elsalamouny et al., 2017).

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The separation of lanthanides utilizing different methods, including solvent extraction (Wang et al., 2017); plasma separation (Gueroult et al., 2018); hydrothermal (Josso et al., 2018), alkaline, and acid extraction (King et al., 2018); adsorption (Awual et al., 2013); and biosorption (Das & Das, 2013; Fomina & Gadd, 2014; Sadovsky et al., 2016; Elsalamouny et al., 2017) has been reported. In principle, precipitation and solvent extraction methods have technical limitations for treating a contaminated aqueous solution; for example, they require some pre-treatments involving physical and chemical processes. Currently, adsorption method using agricultural waste as an adsorbent for the removal of metal ions has been considered as an alternative and effective method of recovering the metal ions (Das & Das, 2013; Bhatnagar et al., 2015; Elsalamouny et al., 2017; Omo-Okoro et al., 2018;). On the other hand, adsorption method with biomaterials, such as microorganisms and biomass wastes, where adsorbates are bound by the active sites of the biomaterials have also attracted wide attention (Fomina & Gadd, 2014). Agricultural wastes, such as peels from citrus, bananas, cassavas, jackfruits, pomegranates, and garlic, have been explored as an adsorbent, and they offers advantages which surpass commercially available activated carbon via its large surface area, high adsorption capacity, high reactivity, and low cost (Omo-Okoro et al., 2018; Bhatnagar et al., 2015).

Banana peels are an example of fruit wastes that may be practically used as an adsorbent, as its adsorption capacity has been investigated in the separation of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} (Annadurai et al., 2013); strontium (II) (Mahindrakar & Rathod, 2018); and palm oil mill effluent (POME) (Mohammed & Chong, 2014). Considering the capacity of banana peel as adsorbents for metal separation, this biomass has the potential to separate lanthanides from bauxite tailing waste. In this study, banana peels (*Musa paradisiaca L.*) was selected as an adsorbent, as it consists of organic carbons, such as pectin (10–21%), lignins (6–12 %), cellulose (7.6–9.6 %), and hemi-cellulose (6.4–9.4 %) on a dry basis (w/w) (Mohapatra et al., 2010). The rare metal ions of Y, La, Ce, Nd, and Sm were selected as the model of multicomponent lanthanides with trivalent state in an aqueous solution. The recovery of these metal species from non-conventional resources, such as low-grade bauxite, is a strategic target to extract lanthanide ions. The increase in the demand for lanthanides on the international market and limited resources for their production highlights the importance of the recovery of these rare earth metal elements in this study.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbents

Adsorbents from banana peels are synthesized according to the procedure reported by Mohammed and Chong (2014) with slight modification. Banana peels were collected from Pondok Cina (Indonesia) and were cut into small pieces (1–2 cm), followed by washing once with tap water and further with distilled water to remove external dirt. Wetted banana peels were dried in an oven for 24 h at 110°C. Then, the dried peels were ground with a pulverizer mill blender and homogenized to 250 μm with a sieve shaker. The pulverized peels were carbonized at 400°C for 1 h in a furnace, and then the char was cooled at room temperature. It was then imbibed in a NaOH 45% solution for 16 h at room temperature. The solution was filtered and dried in an oven for 24 h at 110°C, and the activated char was placed in a furnace at 500°C for 1 h. The material was then washed and filtered using cold, distilled water until the pH reached 7. The wetted materials were dried for 8 h at 110°C. The activated carbon adsorbent was obtained and kept for further characterization and application.

The mixture of lanthanide salts, including Y, La, Ce, Nd, and Sm nitrate were used as representative models to evaluate the adsorption properties in the multicomponent system. The solutions of each lanthanide nitrate was weighed and then dissolved in 1,000 mL of distilled water to obtain a concentration of 0.7 mmol/L for each salt. The initial concentration of each Ln^{3+} was

fixed at 0.7 mmol/L and diluted in distilled water. In total, 100 mg of the adsorbent was added to 50 mL of each lanthanide solution and stirred at 200 rpm for a period ranging from 0.5 to 2.5 h, with a time span variation of 0.5 h. The pH of the lanthanide solutions was adjusted using 0.1 M HCl or NaOH.

Low-grade bauxite was collected from Wacopek, Riau Island (Indonesia), and it was ground and sieved to a particle size of 200 mesh. The ground low-grade bauxite was then diluted in distilled water until it reached an initial concentration of 1,500 mg/L. The pH of the solution was adjusted using 0.1 M HCl.

The adsorption of lanthanide ions in solutions was studied in batch experiments. For the equilibrium time study, the lanthanide solution was mixed with activated carbon using a magnetic stirrer for 0.5 to 2.5 h at room temperature. For the pH-edge experiment, the initial pH of the solution varied from 3 to 5. The equilibrium time and pH which yielded the maximum (%) adsorption of lanthanide ions was evaluated for the low-grade bauxite sample. The mixture was filtered, and the concentration of lanthanide metals was determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

The removal (%) of each lanthanide element was determined using the following mass balance:

$$\text{Percentage of removal} = \frac{C_0 - C_t}{C_0} x100\% \quad (1)$$

where C_0 and C_t are the initial and final concentrations, respectively, of lanthanide metal ions (mg/L).

2.2. Characterization

The sample surface areas were characterized using multipoint adsorption-desorption isotherm results at 77 K with a Brunauer–Emmett–Teller (BET) model. The ASAP 2020 V4.02 (Micromeritics, US) analyzer used an equilibration time interval of 5 s, no low-pressure dose, and an analysis bath temperature of 77 K. Prior to the BET analysis, the sample was subjected to degassing under a high vacuum at 350°C for 4 h. The concentration of lanthanide metals was analyzed using ICP-OES.

3. RESULTS AND DISCUSSION

3.1. Surface Area Characterization of Adsorbent

The characterization of BET aims to determine the surface area of all three types of adsorbents; the pore size and volume, if any; and the average particle size. The BET characterization result is presented in Table 1.

Based on the BET test results, it can be seen that the activated carbon adsorbent has an area 100 times larger than that of the natural adsorbent. This shows that carbon activation was successful. A larger surface area is observed due to the presence of pores formed upon activated carbon formation. Pectin adsorbents have a slightly larger surface area than natural adsorbents, and they do not have pores. The purpose of the esterification treatment of banana peels is to obtain pectin compounds, not activation, so pores were not formed and the surface area tends to be in an uncharged neutral state as for the case of natural adsorbents without modification. These differences are due to the behavior of molecule and nitrogen adsorption data due to the similar and/or different physicochemical properties of the molecular size and polarity, among other reasons (Wilson & Mahmud, 2015).

Compared with the results of the iodine test, the BET surface area has a much smaller value. However, the trend for the results are consistent on a relative scale as revealed by the large surface

area of active carbon followed by pectin and natural (pristine) materials. A smaller BET surface area might have been caused by low micropore volume or limited N_2 adsorption at surface inaccessible micropores, as inferred from the results in Table 1.

The BET surface areas for a natural adsorbent, pectin, and activated carbon are about 24.25 m^2/g, 162.36 m^2/g, and 875.29 m^2/g, respectively, as reported (Mohammed & Chong, 2014). This suggests that the adsorbents prepared by researchers are no better than those reported by Mohammed and Chong (2014). Several factors that led to the effect are illustrated by the case of esterification and the type of carbon activation. Esterification was conducted recently within 16 h, while Mohammed and Chong (2014) conducted esterification for 48 h. The longer the esterification, the greater the yield of pectin produced. However, it does not cover the possibility that with longer esterification, the yield of pectin might reach a maximum and then saturate due to decarboxylation (de Oliveira et al., 2016).

The activation of carbon often covers a temperature range of 400–500°C and the use of NaOH. By contrast, Mohammed and Chong (2014) used a higher temperature (500–700°C) and KOH as an activator. KOH and NaOH are commonly used for carbon activation, where KOH is a stronger base than NaOH. Increasing the temperature of carbonization after impregnation heating accelerates the degradation of the precursor, where the pore surface area increases at some point and decreases after the equilibrium temperature is reached (Sudaryanto et al., 2006). Sudaryanto et al. (2006) investigated the effect of the impregnation ratio and carbonization temperature as a function of the BET surface area for the preparation of activated carbon from cassava peel by chemical activation. Sirimuangjinda et al. (2013) compared the use of NaOH and KOH as activators for activated carbon preparation. The activation of carbon using KOH results in a larger surface area than activation with NaOH.

Table 1 BET characterization of natural, pectin, and activated carbon from banana peels

Parameter	Natural	Pectin	Activated Carbon
Surface area (m^2/g)	0.32	0.40	32.84
Pore volume (cm^3/g)	-	-	0.04
Pore size (nm)	-	-	8.05
Particle size (μm)	18.5	14.9	18.3

3.2. Iodine Number

Table 1 shows that activated carbon has the highest iodine absorption and surface area. Activation or oxidation produces a porous structures that provides a larger surface area, and the ability to adsorb the substance increases. Investigating the iodine number for absorption involves determining the ability of activated carbon to adsorb materials in a solution.

Table 2 Iodine test of natural, pectin, and activated carbon from banana peels

Type of Adsorbent	Iodine Number (mg/g)	Surface Area (m^2/g)
Natural	470.11	469.03
Pectin	526.88	559.05
Activated Carbon	572.18	630.87

3.3. Adsorption Study

Figure 1 presents the equilibrium time required for Ln^{3+} adsorption using activated carbon from banana peels. The equilibrium time for adsorption is reached at 2.5 h. The rate of lanthanide

adsorption was higher at times before 1 h and then became relatively constant thereafter. This may be due to the active sites in adsorbents that are vacant in the early stages of the isotherm profile. Along with the adsorption duration that passed, the vacant sites of the adsorbent will be filled by lanthanides and produce a constant level of adsorption because there is no active side that can bind the lanthanides again. The difference in the concentration of lanthanide ions between the solution and the adsorbent at the beginning is significant and will decrease as adsorption occurs, so mass transfer occurs progressively in the beginning stages and is lower or even constant as the system reaches equilibrium.

3.3.1. The effect of time

The mixture was stirred because stirring in the aqueous system raises the adsorption of lanthanide ions by minimizing mass transfer resistance, while greater rates of stirring may result in mechanical damage to the adsorbent (Fomina & Gadd, 2014). Stirring at 200 rpm was considered appropriate according to the results reported by Mohammed and Chong (2014). In this study, the time interval to determine the equilibrium time varied from 0.5–2.5 h. Figure 1 shows the equilibrium time for the adsorption of lanthanide ions using activated carbon from banana peels. The optimum adsorption time was found to be 2.5 h. This differs from the optimum adsorption time for Sm and Ce ions in sulfuric acid solutions on nanomodified activated carbon (60 min) (Burakova et al., 2018). It also differs from the removal of nickel(II) ion using banana peels (120 min) and coconut shells (30 min) (Olufemi & Eniodunmo, 2018).

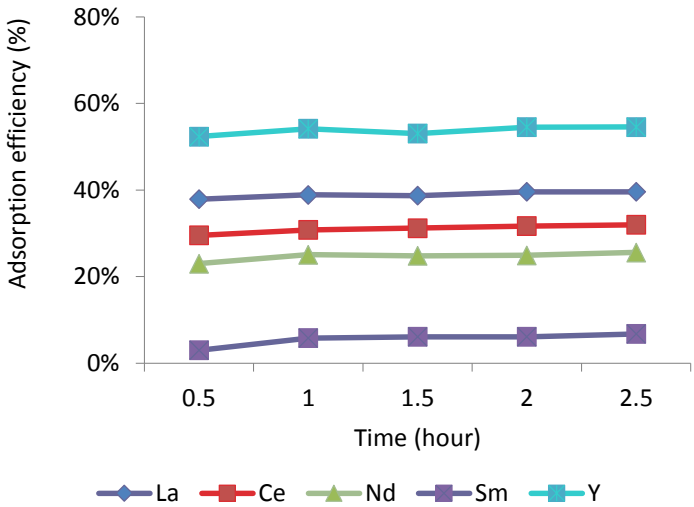

Figure 1 Equilibrium time for lanthanide adsorption using activated carbon from banana peels

3.3.2. Effect of pH

The volume of the lanthanide ion solution samples was 50 mL, where a variable amount of 0.1 M HCl was subsequently added. The pH values varied accordingly (pH = 3.4 and 5). A pH of 5 indicates the typical pH of a commercial lanthanide solution. Figure 2 presents the effect of pH on the adsorption of La ions using activated carbon from banana peels.

Figure 2 shows that the maximum adsorption of La ions was achieved at pH 4. For example, the adsorption percentages (%) are given as follows: Y (31.1), La (40.8), Ce (33.2), Nd (7.6), and Sm (26.2). The lanthanide reactivity to activated carbon from banana peels is La> Ce> Y>Nd> Sm. A similar trend was observed with the adsorption of trivalent La, Ce, and Nd ions using biochar composites, with the maximum removal of lanthanide ions being achieved at an adsorbent dosage of 0.1 g, pH of 4, and contact time of 360 min (Kolodyńska et al., 2018). After the adsorption process, the equilibrium pH reached 4. This was also similarly observed with Cd adsorption using

activated carbon from banana peels (Mohammad et al., 2015). We noted that minimal adsorption at a low pH may be due to competition between H^+ and lanthanide ions for binding to the active sites of the activated carbon adsorbent. Increasing the pH leads to a reduction in H^+ in the solution, so the lanthanide ions have less competition for binding to the active site of activated carbon.

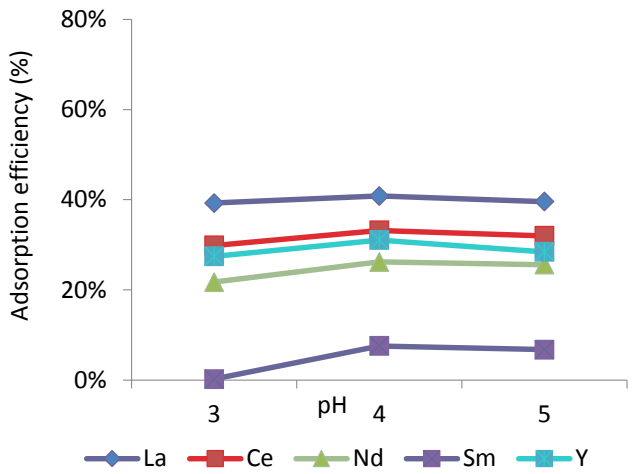

Figure 2 Effect of equilibrium pH time on the adsorption of lanthanide ions by activated carbon from banana peels

3.4. Adsorption of Lanthanide Ions in Low-grade Bauxite

Low-grade bauxite (200 mesh) was dissolved in distilled water with a concentration of 1,500 mg/L, in conformity with the adsorption model of commercial lanthanide metal ions. The pH of the solution was adjusted to 4. The adsorption test was carried out for 2.5 h, according to the equilibrium time of the adsorption model of commercial lanthanide metal ions. Figure 3 presents the adsorption of lanthanide ions from low-grade bauxite at a pH of 4, a time of 2.5 h, and an activated carbon dosage of 100 mg.

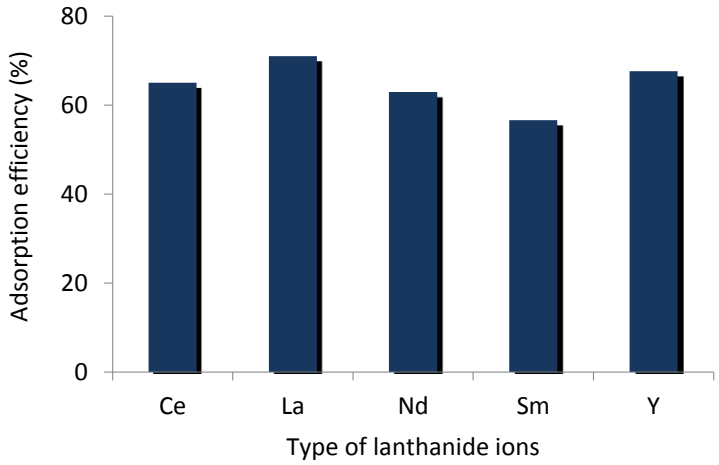

Figure 3 Adsorption of lanthanide ions from low-grade bauxite using activated carbon at a pH of 4, a time of 2.5 hours, and an activated carbon dosage of 100 mg

Figure 3 shows that lanthanum has the highest percentage of removal, followed by Y, Ce, Nd, and Sm. We assumed that the reactivity and binding between lanthanide ions and functional groups on the surface of activated carbon were variable. When compared to the removal (%) due

to the variation in contact time and pH for commercial lanthanides, the removal (%) of lanthanides from low-grade bauxite is noticeably higher. Raising the initial concentration of the pollutant will increase the quantity of pollutants absorbed per unit mass from the adsorbent, but it will decrease the lifting efficiency (Fomina & Gadd, 2014). Lanthanum (La) is a lightweight lanthanide metal that makes it easier to bind to the activated carbon adsorbent. The Y^{3+} ion is capable of competing with the Ce^{3+}, Nd^{3+}, and Sm^{3+} ions for easy binding with adsorbents because of its smaller atomic size and heavy metal properties. We noted that adsorbent materials containing carboxyl and hydroxyl groups afford the adsorption of lanthanide ions over a large pH range, in agreement with the results reported by Iftekhar et al. (2018).

4. CONCLUSION

In this study, activated carbon derived from banana peels was synthesized and evaluated as an adsorbent for the removal of lanthanide ions. BET and iodine number were used to determine its characteristics. The recovery of lanthanide ions from low-grade bauxite was studied at a time of 2.5 h, a pH of 4, and a fixed dosage of 100 mg of the activated carbon adsorbent. The recovery (%) of lanthanide ions from low-grade bauxite is given as follows: Y (67.60), La (71.00), Ce (65.0), Nd (62.93), and Sm (56.59).

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