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APPLICATION OF ACID MODIFIED RED MUD FOR LEAD ION REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT

In this study, the Pb(II) adsorption experiments with the single acid modified red mud were conducted as a function of initial pH, adsorbent doses, contact time, initial Pb(II) concentrations, and competitive ions. The adsorption results pointed that the highest Pb(II) removal efficiency was achieved at the initial pH 4.0, adsorbent dose 7.5 g/L, shaking speed 150 rpm and contact time around 60 minutes at the room temperature. The adsorption results arrowed that the Pb(II) removal efficiency of the modified red mud was enhanced to 150% compared to the raw red mud. The adsorption capacity of the modified red was measured of 9.52 mg/g, higher compared to several previous studies using the same method and type of acid. The study also indicated that the Pb(II) adsorption kinetic and isotherm were best described by the Pseudo - second - order kinetic and fitted to linearly transform both Langmuir and Freundlich with correlation coefficient (R^2) over 0.99. The data obtained in this study indicated that modified red mud by using acid can be used as an effective and low cost adsorbent for heavy metals removal from wastewater.

Keywords: red mud, modified red mud, lead ion removal, heavy metals removal.

1. INTRODUCTION

In the past 15 years, the world's bauxite mining has been grown strongly. It is predicted that the total of bauxite produced in 2014 rise up to 234 million tones. There was an increased 216 % compared to 108 million tons of bauxite produced in 1999 [2]. Based on the calculation of European Alumina Association in 1999 [3], to produce one ton of extracted bauxite, one to

three tons of red mud will be generated. It means the total amount of red mud generated worldwide may reached up to 702 million tones. China, India, and Australia are the largest red mud generation sources with more than 50 % of the total amount of worldwide red mud generation [4]. However, the previous studies have showed that the modified red mud can be used as alternative and effective adsorbent for removal of contaminants from aqueous solution such as heavy metal ions As(III, V) [5], Cd(II) [6, 7], Pb(II) [1, 8, 9,10, 11,12,13] as well as the other contaminants PO_4^{3-} [14] due to the chemical components in red mud such as Fe_2O_3, $Al(OH)_3$, FeO(OH), γ-FeO(OH), SiO_2, $CaCO_3$, TiO_2, which can play as active sites for contaminants adsorption.

With 5.4 billion tons of bauxite, Vietnam is estimated to hold the world's third largest bauxite ore reserves in the world. However, bauxite mining just has been stared a few years recently with two projects Nhan Co and Tan Rai alumina in the Central Highland of Vietnam. Based on the designed capacity of these projects, the amount of dry red mud generated is calculated about 1.2 million tons annually [15]. With the purpose of minimizing environmental treatment cost by utilizing the amount of red mud generated annually. This study will present the obtained results from the single acid modification and application of the acid modified red mud generated from Tan Tai alumina company for Pb(II) removal from aqueous waste solution.

2. MATERIALS AND METHODS

2.1. Materials

Red mud was collected form Tan Rai Alumina Company, is located in Lam Dong province, Central Highland of Vietnam. The pH and surface area of red mud were measured to be 12.8 and 86 m^2/g, respectively. 92.3 % particle sizes of red mud less than 600 µm. XRD analysis detected that red mud contains the following mineral components: FeO(OH) (50.8 % Wt), Fe_2O_3 (15.9 % Wt), $Al(OH)_3$ (13.6 % Wt), $CaTiSiO_5$(9.0 % Wt), $CaCO_3$ (4.9 % Wt), γ-FeO(OH) (3.8 % Wt), and SiO_2 (2 % Wt). After washing by double distilled water, the pH of red was reduced to around 7.5 and treated by HCl 2M solution within 60 minutes and used as a adsorbent material for lead ion removal.

2.2. Chemicals

All chemicals used in this work (HCl, HNO_3, $Pb(NO_3)_2$, NaOH, Lead standard solution) were analytical grade and produced by Merck (Germany). The Pb(II) working solution with the concentration range of 5.0 - 100 mg/L was prepared from lead nitrate salt $Pb(NO_3)_2$ and diluted by deion water and 5 % HNO_3 solution. The initial pH of Pb(II) solution was adjusted by using NaOH and HNO_3 solutions.

2.3. Experimental procedure

The Pb(II) adsorption experiments were conducted at the room temperature by batch method. A fixed amount of adsorbent (except the adsorbent dose experiments) was added into a series of the 100 mL flask containing 25 mL of Pb(II) solution with the different of concentrations, initial pH, and shaken at 150 rpm. After finishing each adsorption experiments and phases separation by centrifuge, the pH of aqueous solution was measured again to determine the equilibrium pH by using Toledo pH meter. The Pb(II) concentration remains in the adsorbed solution and on the modified red mud were analyzed by using ICP-MS (Inductively

Coupled Plasma Mass Spectroscopy, Canada). The Pb(II) removal efficiency is calculated based on the mass balance equation as follows.

$$H(\%) = \frac{C_o - C_e}{C_o} x100 \quad (1)$$

where: C_o: Initial Pb(II) concentration (mg/L)

C_e:Pb(II) concentration remains in the adsorbed solution at the equilibrium (mg/L)

C_{ad}: the amount of Pb(II) adsorbed on the modified red mud at the equilibrium (mg/g)

The accurate of the efficiency calculation based on the different C_o and total of C_e and Pb(II) adsorbed on the modified red mud at the equilibrium C_{ad} (mg/L) less than 5%.

The change in chemical compositions and surface of the modified red mud before and after adsorption will be determined by XRD and SEM analysis methods (Nova Namo Scaning Electron Microscopy NEP 199).

3. RESULTS AND DISCUSSION

3.1. Effect of initial pH

The pH is the most important factor that effects the adsorption of any metal ions, it decides the existing form of metal ions in the aqueous solution in general, and Pb(II) in particular. Thus, pH was the first influence investigated in the range 0.5 to 5.0 with the fixed adsorbent dose 10 g/L, initial Pb(II) concentration 30 mg/L. The results are presented in Figure 1.

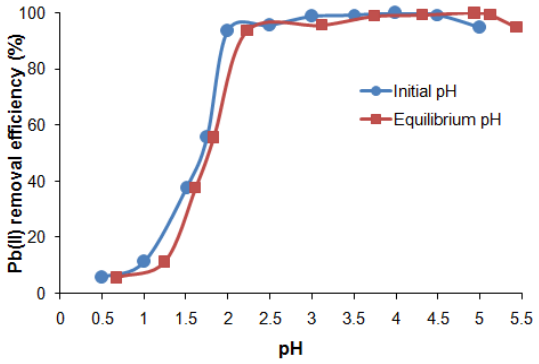

Figure 1. Effect of initial pH on Pb(II) adsorption.

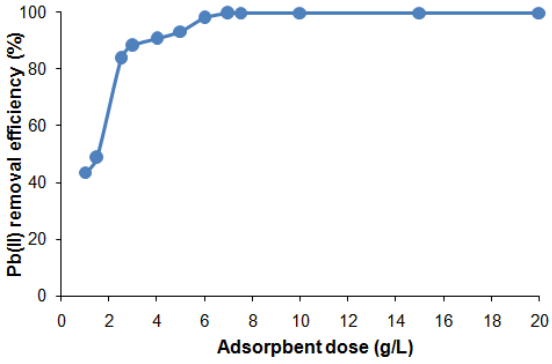

Figure 2. Effect of adsorbent dose on Pb(II) adsorption.

(Initial Pb(II) concentration 30 mg/L, adsorbent dose 10 g/L, temperature 30 ^oC, shaking speed 150 rpm, contact time 2h)

The percentage removal of Pb(II) of the acid modified red mud were found to increase strongly from to 5.73 % to 99.9 % when increase in pH from 0.5 to 4.0. In contrary to the increase phenomena, the decrease in Pb(II) removal efficiency was also found when pH increased to 5.0. The Pb(II) efficiency was calculated to 91.3% only. It means at the pH lower than 4.0 is a better condition for the desorption, and at the pH higher than 4.0 the precipitation occurred and coated around the particles, preventing Pb(II) contact to the surface of red mud and

leading to the decrease in lead ion removal efficiency [16]. The same trend with the rise in Pb(II) adsorption efficiency, the equilibrium pH was also found to increase, due to the residue of $CaCO_3$ in the modified red mud was continued dissolve, the Ca^{2+} in the adsorbed solution was measured 6.4 mg/L. However, the dissolution of $CaCO_3$ was not effective on the Pb(II) adsorption due to the presence of Fe_2O_3, FeO(OH) and $Al(OH)_3$ in the red mud play as the active sites for Pb(II) adsorption [1].

3.2. Effect of adsorbent dose

According to the results were presented in Figure 2**,** the Pb(II) adsorption efficiency was found to increase strongly as there was an increase adsorbent from 1.0 g/L to 7.5 g/L, respectively, because the increase in adsorbent dose will increase the number of active sites. However, it was found that if the adsorbent dose continued increase to 10 g/L or 20 g/L, the Pb(II) adsorption efficiency was found nearly unchanged due to overlapping of active sites. Thus, adsorbent dose 7.5 g/L was considered as optimum dose and used for the next study.

3.3. Effect of contact time

The adsorption rate of Pb(II) was high at the beginning of the adsorption. The percentage of Pb(II) adsorbed was found to increase quickly from 5.0 % to 97.3% for a contact time of 0.5-20 minutes (Figure 3). It may due to the face that adsorption sites are free and Pb(II) interact easily with these sites. After 40 minutes, 99.3% of Pb(II) was removed and the remain of Pb(II) becomes almost constant. This points that the possible monolayer formation of Pb(II) on the outer surface and can be considered as equilibrium time of adsorption time

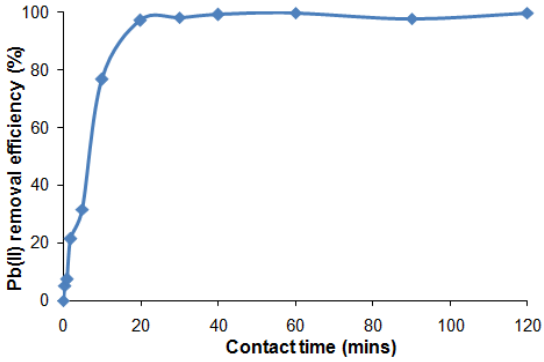

Figure 3. Effect of contact time on Pb(II) adsorption (Initial pH 4.0, initial Pb(II) concentration 30 mg/L, temperature 30 ^oC, shaking speed 150 rpm, adsorbent dose 7.5 g/L).

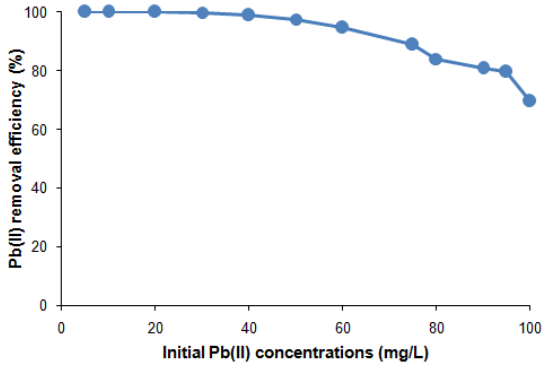

Figure 4. Effect of initial Pb(II) concentration on adsorption efficiency (Initial pH 4.0, temp. 30 ^oC, adsorbent dose 7.5 g/L, shaking speed 150 rpm, contact time 1 h).

3.4. Effect of initial Pb(II) concentrations

The effect of initial Pb(II) concentrations were conducted in the range of 5.0 mg/L – 100 mg/L with the optimum of initial pH and adsorbent dose. The data is presented in Figure 4 showed that in the range of initial Pb(II) from 5.0 mg/L to 40 mg/L, the adsorption efficiency was nearly unchanged. 99.9% of Pb(II) was adsorbed on the surface of the modified red mud. However, at the higher Pb(II) concentrations, the adsorption efficiency was found to decrease. When the initial Pb(II) concentration increased to 100 mg/L, the adsorption efficiency decreased

to 70% only due to the limit of active sites on the surface of red mud when increase in the Pb(II) initial concentration.

According to the SEM images (Figure 5) of acid modified red mud before and after adsorption, it is not difficult to release the different in color and shapes. The rounded shape aggregate particles due to the presence of some mineral phases mainly hematite, and goethite. These mineral components are more soluble in an acidic condition. The images also confirmed that the Pb(II) adsorption occurred on the surface of adsorbent.

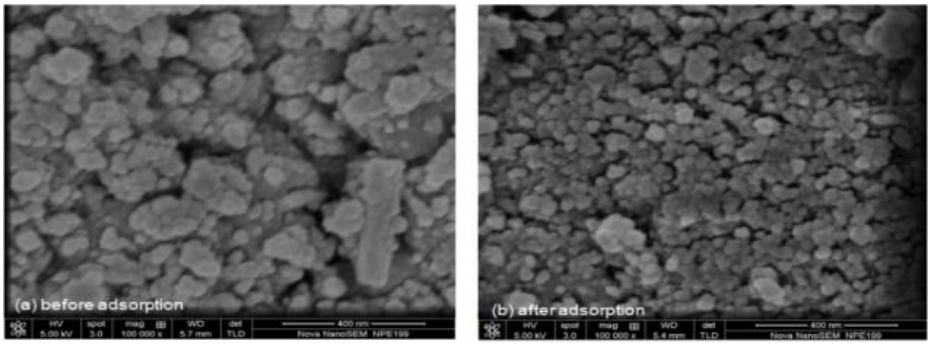

Figure 5. SEM images of the modified red mud before and after Pb(II) adsorption (Initial pH 4.0, initial Pb(II) concentration 30 mg/L, temperature 30 ^{o}C, shaking speed 150 rpm, adsorbent dose 7.5 g/L).

Similar to the modification, The XRD peaks of the acid modified red mud before and after adsorption (Figure 6) indicated that the mainly components hematite Fe_2O_3, goethite FeO(OH),γ-FeO(OH), $Al(OH)_3$. Due to the intensity of gibbsite peak was decreased prominently whereas the peaks intensities. Specially, $CaCO_3$ was not detected on the modified red after adsorption because this component is continued dissolved during adsorption time.

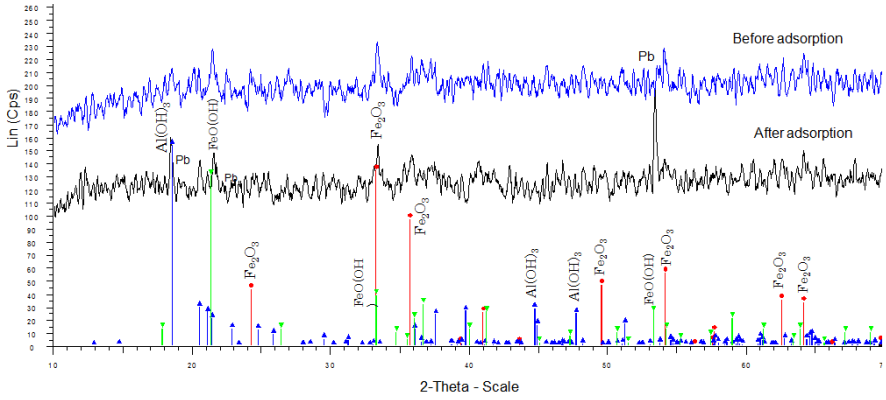

Figure 6. XRD analysis of the modified red mud before and after Pb(II) adsorption (Initial pH 4.0, initial Pb(II) concentration 30 mg/L, temperature 30 ^{o}C, shaking speed 150 rpm, adsorbent dose 7.5 g/L).

3.5. Adsorption isotherm

The linearized Langmuir adsorption isotherm equation which is valid for monolayer sorption onto a surface with finite number of identical sites is as follows:

$$\frac{t}{q_e} = \frac{1}{q_m} bC_e + \frac{t}{q_m} \quad (2)$$

where: C_e: the equilibrium concentration of adsorbate in solution (mg L^{-1}),
q_e: the amount adsorbate adsorbed at equilibrium (mg/g),
q_m: the theoretical maximum adsorption capacity (mg/g),
b: the Langmuir constant (L/mg).

The linear plot of $\frac{1}{C_e}$ versus $\frac{t}{q_e}$ with correlation coefficient R^2 over 0.99 indicates the applicability of Langmuir adsorption isotherm (Figure 7). This indicates a monolayer sorption of lead onto the adsorbent surface. The maximum adsorption capacity (q_m) and binding energy constant (b) of activated red mud for lead was 9.52 mg/g and 3.71 L/mg, respectively according to Langmuir model.

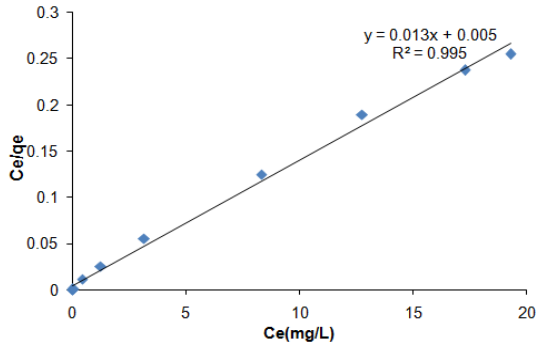

Figure 7. Langmuir isotherms.

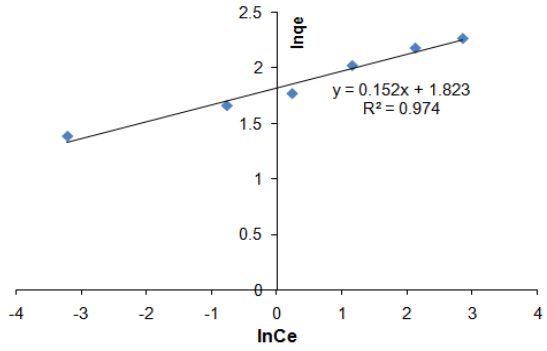

Figure 8. Freundlich isotherm.

Freundlich adsorption isotherm adopts multilayer adsorption on heterogeneous surfaces. Linearized form of the Freundlich equation is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \quad (3)$$

where: q_e: the amount of lead ions adsorbed at equilibrium time (mg/g),
C_e: the equilibrium concentration of lead ions in the solution (mg/L),
K_f: the adsorption capacity (mg/g),
n: an empirical parameter.

The Freundlich isotherm of acid modified red mud is shown in Figure 8.

Table 1. Langmuir and Freundlich isotherms.

Langmuir isotherm			Freundlich isotherm		
q_{max} (mg g^{-1})	B	R^2	N	k	R^2
9.52	3.71	0,997	5.09	5.71	0.974

Comparing correlation coefficient between Langmuir and Freundlich isotherms was shown in Table 1. The higher R^2 (0.995) of Langmuir indicates that the adsorption data prefer follows Langmuir equation than by Freundlich model. However, with the R^2 (0.974) of Freundlich, the adsorption may be also fits both Langmuir and Freundlich isotherms, due to the physical and chemical adsorption of Pb(II) may be occurred simultaneously.

3.6. Adsorption kinetics

The rate constant K_1 for the adsorption of Pb(II) was studied by Lagergren rate equation [17], for initial lead concentration of 30 mg/L.

Pseudo-first-order rate expression of Lagergren equation: $$\log(q_e - q_t) = \log q_e - \frac{K_2 t}{2.203} \quad (4)$$

Where: q_e: The amount of Pb(II) adsorbed at the equilibrium (mg/g),
q_t are the amount of lead adsorbed at time t (min), respectively (mg/g),
K_1 is the Pseudo-first-order rate constant (min^{-1}).

The K_1 and correlation coefficient R^2 were calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus 't' at different time intervals. The K_1 and R^2 were found to be 0.89 and 0.126, respectively.

The Pseudo-second-order rate expression is: $$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \quad (5)$$

Where: K_2 is the Pseudo-second-order rate constant (g/mg.min).

The calculation from the slope and intercept of the plot $\frac{t}{q_t}$ versus time 't' was almost linear shown in Figure 9. The values of K_1, K_2 and R^2 were given in Table 2. The low value of K_2 and high value of R^2 indicates that the adsorptions followed Pseudo-second-order kinetics.

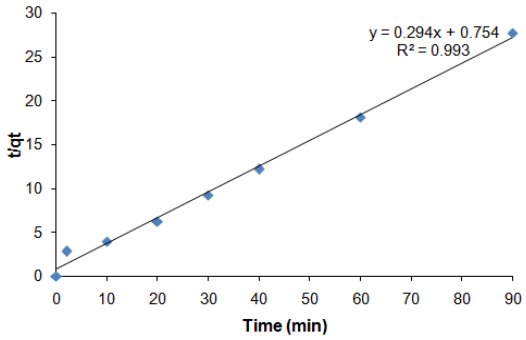

Figure 9. Pseudo – second – order.

Table 2. Kinetics constants and related regression coefficients.

Pseudo 1st order	K_1, min^{-1}	q_e (mg/g)	R^2
	0.126	2.03	0.89
Pseudo 2nd order	K_2 (g/mg. min)	q_e (mg/g)	R^2
	0.051	3.7	0.993

4. CONCLUSIONS

Based on the results presented in this study, the following conclusions can be recommended:

Raw red mud generated from alumina production can be used as a low cost adsorbent for Pb(II) removal from aqueous solution.

The Pb(II) removal efficiency of red mud can be enhanced by the modification using HCl solution. The highest modification efficiency of red mud was achieved with HCl 2M solution. The Pb(II) removal efficiency was increased to 150 % compared to raw red mud at the same adsorption conditions (initial pH 4.0, initial Pb(II) concentration 30 mg/L, temperature 30 ^oC, shaking speed 150 rpm, adsorbent dose 7.5g /L) with the Pb(II) adsorption capacity was 9.52 mg/g.

The optimal adsorption condition for Pb(II) at initial pH 4.0, adsorbent dose 7.5 g/L, shaking speed 150 rpm within 60 minutes at the temperature of 30 ^oC.

The Pb(II) adsorption isotherm and kinetic of modified red mud was fitted to linearly transform both Langmuir and Freundlich, followed the Pseudo-second-order with the $R^2 > 0.97$

After Pb(II) adsorption, the acid modified red mud can be reused by the desorption. However, this framework will be investigated and published in the coming studies.

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