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Original Article

Removal of Pb^{2+} from Aqueous Solution using Thach Khoan Kaolin from Phu Tho Province

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Abstract: Kaolin sample (mixture of halloysite and kaolinite) from Thach Khoan, Phu Tho province was studied to remove Pb^{2+} ions from an aqueous solution. The SEM-EDS and TEM analysis showed that in the kaolin sample, tubular halloysite and plate kaolinite minerals coexist, similar to the results from previous studies. The various treatment conditions such as contact time, solution pH, the adsorbent weight, and initial concentration of Pb^{2+} were examined and evaluated using batch adsorption experiments. The results showed that under experimental conditions of pH_0 = 5.31 and a temperature of 25 °C, with 0.7 g of Thach Khoan kaolin material, the Pb^{2+} adsorption can reach equilibrium after about 50 minutes and efficiency reached 90.75%. The adsorption process follows the Langmuir adsorption isotherm model with the maximum monolayer adsorption capacity of 3.79 mg/g and follows the pseudo-second-order kinetic equation. This result indicated that unmodified Thach Khoan kaolin with a mixture of tabular halloysite and plate kaolinite minerals has a significant potential in removing heavy ions from aqueous solution.

Keywords: Halloysite, kaolinite, tabular, pegmatite, Thach Khoan, Pb^{2+}.

1. Introduction

Vietnam possesses a rich reservoir of kaolin (mixture of halloysite and kaolinite) originated from hydrothermal process - metasomatism, weathering, and re-sedimentation [1]. Several studies have reported the properties, distribution, sources, and potential application of kaolin material [1-5]. Doan Huy Cam et al., (2006) stated that the kaolin reserve in the Northeast Vietnam region is about 85 million tons [2]. The authors have suggested that kaolin weathered

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from pegmatite had good quality to make high-grade ceramics, paper, rubber, and pesticides. Le Do Tri et al., (2008) indicated that the total kaolin reserve/resources of Vietnam are about 268 million tons [3]. However, the authors referred that the research on mineral composition and mineral processing have not been paid much attention, leading to low economic value of this raw material. Additionally, the application aspects of kaolin have not been studied much. Thach Khoan area in Phu Tho province is one of the regions that has many pegmatite bodies belonging to Tan Phuong Complex. Strongly weathered pegmatite bodies provide great potential to form kaolin material in this area. Recently, it is shown that kaolin in Thach Khoan has tabular halloysite, one of the four minerals of the kaolin group [6-8]. Thach Khoan halloysites have a tube-shaped structure with an outer diameter size of over 50 nanometers (nm) and lengths of 250-1250 nm. The proportion of halloysite minerals in kaolin samples (particle size <2 µm) is determined by the method 90% [7].

In recent years, due to its unique properties such as tubular structure, non-toxicity, high mechanical strength, and low price compared to tubular carbon nanoparticles, tabular halloysite has received the attention of scientists. Various applications of tabular halloysite minerals are listed such as in making pharmaceuticals, medicine, food, high-quality materials, agriculture, and treating environment [9-12]. In environmental treatment, halloysites were used to remove heavy metal ions from an aqueous solution with certain efficiencies [13, 14]. Salvatore Cataldo (2018) showed that the adsorption capacity of Pb^{2+} ions from an aqueous solution can reach 6.0 mg/g with the pH range of 3-6 [13]. Yunhui Dong (2012) used commercial halloysite to adsorb Zn^{2+} ions in the aqueous solution. The results showed that with the experimental conditions of the initial solution of 10 mg/L, pH 2-9, the adsorption capacity reached 9.87 mg/g [14]. However, the tube-shaped halloysite material used in these studies was a commercial product with high purity. Natural halloysite can coexist with other minerals, similar to kaolin products in Thach Khoan area. Thus, a mixture of halloysite and kaolinite minerals might have different effect on practical applications compared to pure raw materials.

In this paper, we study the ability to remove Pb^{2+} from an aqueous solution of kaolin extracted from Thach Khoan area of Phu Tho. The results will guide us to more effective application of this kaolin material.

2. Material and Methods

2.1. Preparation of Kaolin Material

The sample was extracted from the mineral processing of Lang Dong kaolin deposit, Thach Khoan. The samples were then homogenized and sieved at 32 µm using wet sieving method. The fraction of <32 µm sample was dried at 60 °C (called Thach Khoan kaolin) and used for experiment.

2.2. Experiment

2.2.1. Determination of the Point of Zero Charge (pH_{PZC}) of Thach Khoan Kaolin Material

The pH_{PZC} value was measured by pH drift method. In this method, 0.25 g of Thach Khoan kaolin powder in 50 mL of 0.01 M KCl solution was shaken for 30 minutes with speed of 400 rpm at room temperature. The initial pH values (pH_0) were adjusted in different values using 0.01 M HCl or 0.01 M NaOH. The mixture was then stirred at 800 rpm for 30 minutes. After equilibration, the pH values of the solutions were measured once again (pH_s). The value of pH_{PZC} was determined by plotting a graph of the difference of pH values against the pH_0 for each case. pH_{PZC} is the pH_0 value when $\Delta pH = 0$.

$$\triangle pH = pH_0 - pH_s \quad (1)$$

2.2.2. Absorption of Pb^{2+}

The experiments were conducted by adding a quantity of Thach Khoan kaolin powder to 50 ml of Pb^{2+} solution. The influence of different physicochemical parameters on the adsorption process was examined. Pb^{2+} solutions with initial concentrations of 20 ÷ 80 mg/L were prepared. The contact time was varied between 10 to 120 minutes. The pH of the solutions was adjusted in the range of 3.00 ÷ 6.78 and the dose of Thach Khoan kaolin material changed from 0.3 to 0.9 g. The mixture was then shaken continuously at 100 rpm using a mechanical shaker at room temperature. After filtration to remove the solid, the remaining concentration of Pb^{2+} was determined by using the inductively inducing plasma-mass spectrometric method (ICP-MS).

The adsorption capacity and the adsorption efficiency were determined by equations (2) and (3):

$$Q = (C_0 - C).V/m \quad (2)$$

$$H = (C_0 - C).100/C_0 \quad (3)$$

Where Q (mg/g) and H (%) represent the adsorption capacity and removal efficiency of Pb^{2+}, respectively. C_0 (mg/L) and C (mg/L) are the initial and equilibrium concentrations of Pb^{2+} in solution. V (l) is the volume of the adsorbent solution and m is the mass of Thach Khoan kaolin powder (g), respectively.

The Pb^{2+} adsorption capacity of Thach Khoan kaolin material was calculated based on the isothermal adsorption of Langmuir and Freundlich [15-18].

Langmuir linear equation:

$$\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{K_L.Q_m} \quad (4)$$

Freundlich linear equation:

$$LnQ = LnK_F + \frac{1}{n}.LnC_e \quad (5)$$

Where C_e (mg/L) is the equilibrium concentration of Pb^{2+}, Q (mg/g) is the amount adsorbed at equilibrium. Q_m (mg/g) is the maximum adsorption capacity, K_L is the Langmuir coefficient related to the adsorption energy. K_F and n are the constants of the Freundlich model.

The adsorption kinetics was studied by two kinetic models: the pseudo-first-order model (equation 6) and the pseudo-second-order model (equation 7):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$t/Q_t = t/Q_e + 1/(k_2.\ Q^2_e) \quad (7)$$

Where Q_e is the adsorption capacity at equilibrium (mg/g), Q_t is the adsorption capacity at time t (mg/g). k_1 and k_2 are pseudo-first-order (1/min) and pseudo-second-order (g/mg/min) rate constants, respectively.

2.3. Analytical Methods

X-ray Diffraction (XRD) data was analyzed using Joint Committee of Powder Diffraction Standards (JCPDS) to identify the minerals existing in the sample. The morphology and chemical compositions of the minerals were analyzed using the Scanning electron microscope with Energy-dispersive X-ray spectroscopy (SEM-EDS), Transmission electron microscope (TEM), and Inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and Discussion

3.1. Characteristics of Thach Khoan Kaolin

Figure 1a shows the Thach Khoan kaolin material (<32 µm) that has been dried. XRD pattern showed that both halloysite and kaolinite minerals exist in the sample (Figure 1.a_1). The typical morphologies of these minerals are clearly shown through SEM and TEM images. SEM image in Figure 1B presents that halloysite minerals in rod-shaped shape overlap to form a clear cotton layer (Figure 1b). Figure 1c shows a typical crystal of a plate-type kaolinite mineral. This form is different from that of the tubular halloysite mineral. The EDS results for these minerals indicate the presence of aluminum (Al), silicon (Si), and oxygen (O) elements, corresponding to the chemical formula of the kaolin group ($Al_2Si_2O_5(OH)_4.nH_2O$) (Figure 1d). Figure 2 shows TEM images of tabular halloysite minerals with different magnifications. This is a typical form of the tubular halloysite mineral. Thus, the results of this study indicate the existence of tubular halloysite mineral along with the plate-type kaolinite mineral in the Thach Khoan kaolin sample, consistent with the previous studies [6-8].

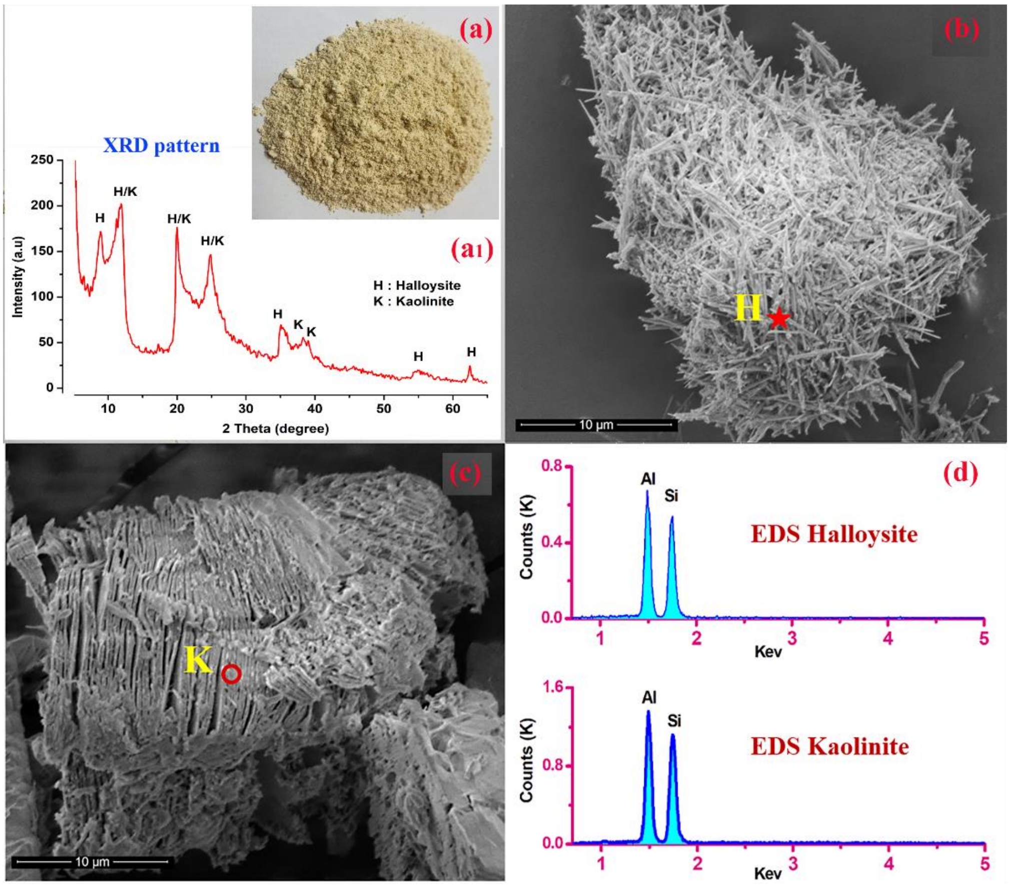

Figure 1. Thach Khoan kaolin powder (a); XRD pattern of the sample (a_1); SEM image of halloysites (b) and kaolinites (c) in the sample; EDS results (d) of Halloysite (H) and Kaolinite (K).

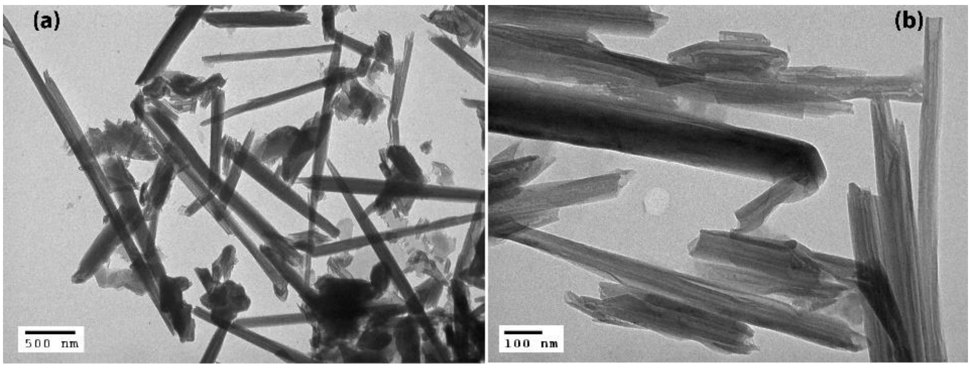

Figure 2. TEM images of tabular halloysites at Thach Khoan area in the different scale bars (500 nm in the left image (a); 100 nm in the right image (b)).

3.2. Determination of pH_{PZC} of Thach Khoan Kaolin

The change of ΔpH against the pH_0 is shown in Figure 3. From the graph, we found that ΔpH = 0 when the pH_0 value is 5.99. This means that the pH_{PZC} value of the Thach Khoan kaolin material is 5.99.

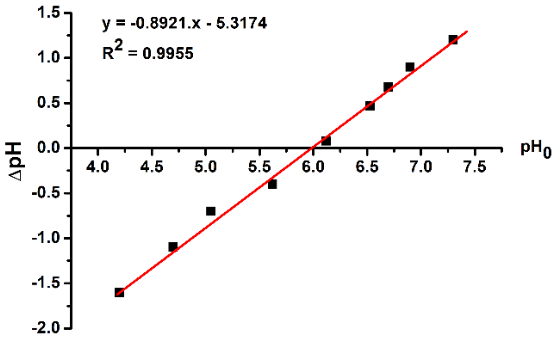

Figure 3. Determination of pH_{PZC} of Thach Khoan kaolin powder.

3.3. Effect of the Experimental Factors on Pb^{2+} Treatment Process

3.3.1. Effect of Contact Time

The effects of the contact time on the Pb^{2+} adsorption capacity and the removal efficiency of 0.5 g of Thach Khoan kaolin against time are shown in Figure 4. The results show that the adsorption capacity and the removal efficiency increase with the increase of the contact time. The adsorption capacity and the removal efficiency increase rapidly during the first 50 minutes and then increase slowly and become steady because the adsorption process has tended to reach an equilibrium state. Therefore, to obtain high adsorption capacity and removal efficiency, a contact time of 50 minutes is selected for the next experiments.

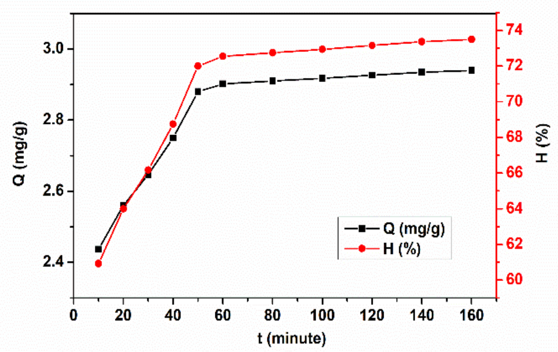

Figure 4. The variation of Pb^{2+} adsorption capacity Q (mg/g) and the removal efficiency H (%) according to contact time (t) m_{kaolin} = 0.5 g; C_0 = 40 mg/L; pH_0 = 5.31; T = 25 °C.

Table 1. The variation of Pb^{2+} adsorption capacity Q (mg/g) and the removal efficiency H (%) according to the pH of the initial solution in conditions of m_{kaolin} = 0.5 g; C_0 = 40 mg/L; t = 50 min; T = 25 °C

pH value	Initial concentration (Co) (mg/L)	Equilibrium concentration (C) (mg/L)	Removal efficiency (H) (%)	Adsorption capacity (Q) (mg/g)
3.00	40	18.32	54.20	2.16
3.95	40	15.37	61.58	2.46
4.96	40	14.11	64.73	2.58
5.31	40	11.20	72.00	2.88
5.58	40	10.74	73.15	2.92
5.95	40	8.21	79.48	3.18
6.40	40	4.00	90.00	3.60
6.78	40	1.37	96.58	3.86

3.3.2. Effect of pH

The removal of Pb^{2+} ions from an aqueous solution depends on the pH of the solution because pH changes the surface properties of the adsorbent. With pH_{PZC} = 5.99, the experiments were carried out at a pH of 5.99. However, to avoid precipitation of $Pb(OH)_2$ in an alkaline environment (pH > 7.5), the effect of pH has been investigated with a pH ≤ 7. The results of the variation of the Pb^{2+} adsorption capacity and the removal efficiency of Thach Khoan kaolin material are presented in Table 1. In the pH range of 3 to 6.78, the Pb^{2+} adsorption capacity Q (mg/g) and the removal efficiency H (%) increase with the increase of pH values. This phenomenon is caused by the fact that halloysite minerals are protonated and their surface is positively charged, resulting in a decrease in the number of adsorption sites. Also, there is an adsorption competition between H^+ and Pb^{2+} ions, which decreases the adsorption capacity of Thach Khoan kaolin material. Thus, the range of pH = 5.31 ÷ 6.78 is suitable and can be selected. However, to facilitate the treatment process, especially the treatment with large quantities, the natural pH (≈ 5.3) is selected for further investigations.

3.3.3. Effect of Adsorbent Mass

The effect of the mass of Thach Khoan kaolin powder on the adsorption capacity and removal efficiency of Pb^{2+} is shown in Figure 5. It indicates that when the mass of Thach Khoan kaolin material increases from 0.3 to 0.7 g, the adsorption capacity decreases from 3.13 to 2.59 mg/g, and the removal efficiency increased rapidly from 47% to 90.75%. When the mass of the adsorbent increases to 0.9 g, the removal efficiency increases slowly to 93.75%. To obtain a high combined adsorption capacity and removal efficiency, the mass of Thach Khoan kaolin material of 0.7 g is selected for the treatment of Pb^{2+} from the aqueous solution.

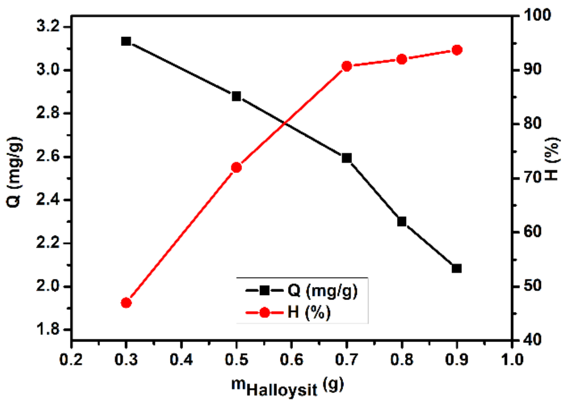

Figure 5. Effect of Thach Khoan kaolin mass on adsorption capacity Q (mg/g) and the removal efficiency H (%) at conditions of C_0 = 40 mg/L; pH_0= 5.31; t = 50 mins; T = 25 °C.

3.4. Adsorption Isotherm

The optimal experimental conditions for removal of Pb^{2+} from aqueous solution are 0.7 g of kaolin material, a contact time of 50 minutes, a pH_0 value of 5.31 at room temperature (25 °C). The initial concentration range of Pb^{2+} is from 20 to 80 mg/L.The remaining Pb^{2+} concentration at equilibrium (Ce), the values of lnC_e, lnQ, and the C_e/Q ratio are shown in Table 2 and Figure 6.

Table 2. The values of lnC_e, lnQ and C_e/Q ratio determined from the different initial concentration of Pb^{2+}

C_o (mg/L)	C (mg/L)	Ln Ce	Q (mg/g)	LnQ	Ce/Q (g/l)
20	0.40	-0.92	1.40	0.34	0.29
30	1.27	0.24	2.05	0.72	0.62
40	3.70	1.31	2.59	0.95	1.43
50	6.98	1.94	3.07	1.12	2.27
60	13.78	2.62	3.30	1.19	4.17
70	19.95	2.99	3.58	1.27	5.58
80	28.66	3.36	3.67	1.30	7.82

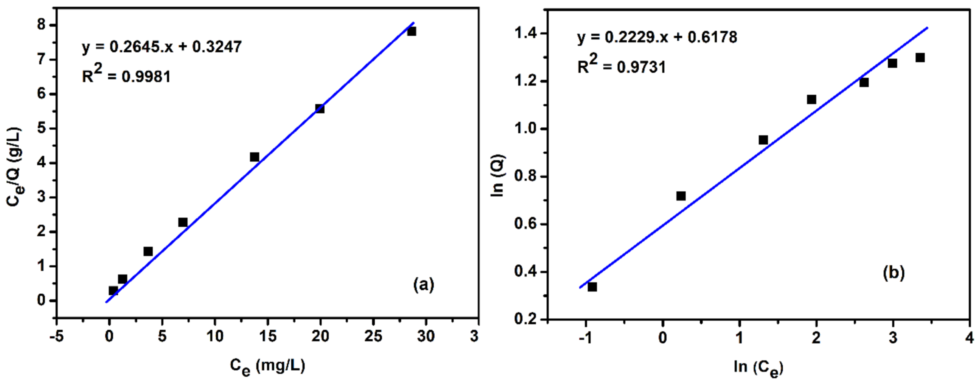

Figure 6. Adsorption isotherm curves at 25 °C follow (a) Langmuir and (b) Freundlich models.

From Table 2, the adsorption isotherm curves are established according to the Langmuir adsorption isotherms (equation 4) and Freundlich (equation 5) (Figures 6a and 6b). Based on these adsorption isotherm curves, both Langmuir and Freundlich adsorption constants can be calculated, respectively and the result is shown in Table 3. From the results, the Pb^{2+} adsorption on Thach Khoan kaolin material can be described by both Langmuir and Freundlich isothermal adsorption models. However, it can be seen that the R^2 value of the Langmuir isothermal model (R^2 = 0.9981) is higher than that of the Freundlich model (R^2 = 0.9731) with the maximum adsorption capacity of 3.79 mg/g. It indicates that the Langmuir isotherm is more appropriate than the Freundlich isotherm in describing the adsorption of Pb^{2+} ions on Thach Khoan kaolin.

Table 3. Experimental constants *Q*m, K_L, K_F, and *n* in Langmuir and Freundlich equations

Langmuir isothermal model		
Q_m (mg/g)	K_L	R^2
3.79	0.75	0.9981
Freundlich isothermal model		
n	K_F	R^2
4.49	1.85	0.9426

3.5. Adsorption Kinetics

By varying the reaction time, the graphs of pseudo-first-order (Figure 7a) and pseudo-second-order (Figure 7b) kinetic equations are established.

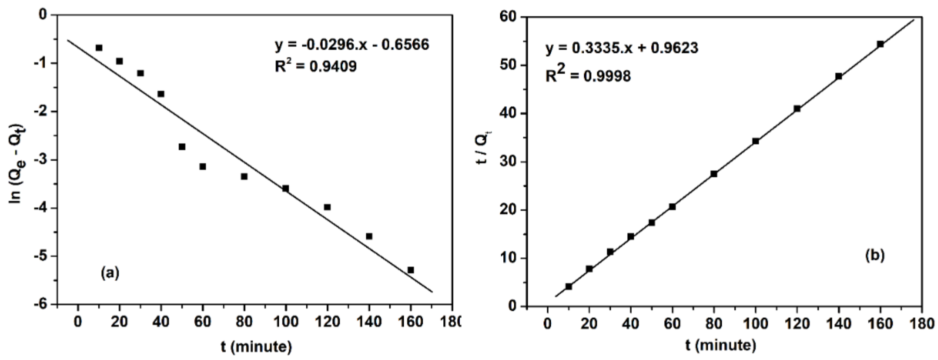

Figure 7. The description of the experimental data by (a) pseudo-first-order and (b) pseudo-second-order kinetic equations.

Table 4. The values of *k* and Q_e calculated from pseudo-first-order and pseudo-second-order kinetic equations.

Pseudo-first-order kinetic equation			Pseudo-second-order kinetic equation			Experimental Q_e (mg/g)
Q_e (mg/g)	k_1 (1/min)	R^2	Q_e (mg/g)	k_2 (g/mg/min)	R^2	
0.971	0.0296	0.9409	2.999	0.116	0.9998	2.945

From Figure 7, the adsorption rate constants (k) and the equilibrium adsorption capacity (Q_e) are calculated (Table 4). Q_e value calculated from the pseudo-first-order kinetic equation (0.971 mg/g) is much smaller than the experimental Q_e value (2.945 mg/g). Meanwhile, the Q_e calculated from the pseudo-second-order kinetic equation (2.999 mg/g) is similar to the experimental Q_e value (2.945 mg/g). In this case, the regression coefficient R^2 = 0.9998, approximately equal to 1. It indicates that the experimental data fit well into the pseudo-second-order model, suggesting that it can be used for the Pb^{2+} adsorption process by Thach Khoan kaolin material.

4. Conclusions

The purpose of this study was to expand the applications of natural kaolin from Thach Khoan, Phu Tho province. The sample was collected after mineral processing and then separated to the particle size of <32 µm by the wet sieving method. The analysis results of SEM-EDS and TEM both showed that the kaolin sample existed mainly with tubular halloysite and a part of plate kaolinite minerals.

The results of using this kaolin material to study the Pb^{2+} adsorption process in an aqueous solution show that the adsorption process is influenced by the following factors pH, contact time, the mass of kaolin material. Under experimental conditions of pH_0 = 5.31 and a temperature of 25 °C, with 0.7 g of kaolin material, the Pb^{2+} adsorption can reach nearly equilibrium after about 50 minutes with 90.75% of efficiency reached. The adsorption process follows the Langmuir adsorption isotherm model with the maximum monolayer adsorption capacity of 3.79 mg/g and follows the pseudo-second-order kinetic equation. This result showed the potential of applications of natural kaolin in this area, especially in environmental treatment.

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