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Removal of heavy metal ions from wastewater by combined modified kaolin

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ABSTRACT

The removal of lead Pb (II) and cadmium Cd (II) from wastewater by using three different types of kaolin including natural kaolin, sodium hydroxide NaOH-modified kaolin, and NaOH-calcination-modified (combined modified) kaolin was studied. Textural properties of the three types of kaolins were characterized by scanning electron microscopy, fourier transform infrared spectroscopy, and specific surface area analysis. The effects of calcination temperature, contact time, adsorption temperature, pH, and kaolin dosage were investigated. Results showed that NaOH-calcination-modified kaolin performed best among the three kaolins in removing Pb (II) and Cd (II). Compared to NaOH-modified and natural kaolin, the shape of combined modified kaolin was irregular, and its surface was rough and loose with bigger pore volume. The adsorption capacity of Pb (II) and Cd (II) could reach the maximum of 161.84 and 108.13 mg g^{-1}, respectively, under the following condition: initial concentration of heavy metals ions was 200 mg L^{-1}, pH was 5.5, adsorption temperature was 25°C, contact time was 60 min, and NaOH-calcination-modified kaolin dosage was 1 g. Combined modified kaolin was also applied to remove heavy metal ions from actual industrial wastewater samples, and the results demonstrated that modified kaolin is a type of useful adsorbent for the removal of heavy metals from wastewater. Furthermore, the adsorption process of kaolin on Pb (II) and Cd (II) conformed to first and second-order kinetics equation, respectively.

Keywords: Sodium hydroxide-calcination-modified kaolin; Lead(II); Cadmium(II); Adsorption mechanism; Wastewater treatment

1. Introduction

Heavy metals contamination in environment has caused extensive ecological and public health concern throughout the world. With economic development, wastewater contaminated with heavy metal ions is increasingly produced during industrial processes and directly or indirectly discharged into the environment especially in developing countries [1–3]. Unlike organic contaminants, heavy metals are non-biodegradable and tend to accumulate in living organisms posing serious health hazards as they are toxic or carcinogenic. Lead Pb (II) and cadmium Cd (II) are the two common water pollutants which are derived from industrial processes such as battery production and printing and dyeing process [4–6]. They are harmful to human health as they are capable of damaging human nervous system, digestive system, hematopoietic system, and reproductive system [7,8]. Therefore, in order to prevent the humans and environment, removal of these toxic heavy metal ions from wastewater is highly desirable.

In recent years, numerous methods such as chemical precipitation, electrolysis, and adsorption [9–11] have been developed for the treatment of wastewater containing heavy metal contaminants. Natural kaolin has attracted progressively more attention of researchers for its low cost and good ion exchange property [12–15]. Ming et al. [16] investigated the natural kaolin to remove heavy metal ions from wastewater and showed that it exhibited the best adsorption performance toward Pb (II) than toward Cd (II), Ni (II), and Cu (II). Ahmet et al. [17] and other researchers also investigated the adsorption of Pb (II) by kaolin. In order to improve the adsorption ability of the natural kaolin

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for heavy metals, some experiments were devoted to modify the surface of kaolin [18–21]. Modified kaolin exhibited better adsorption capacity for heavy metals than natural kaolin [16,22]. Mehmet et al. [23] studied the acid and alkali-modified adsorbents, which could promote the removal of Pb (II) and Cd (II). The adsorption process of Pb (II) on hydrochloric acid (HCl)-activated kaolin was examined in aqueous solutions by Sayed et al. [18], and removal rate of Pb (II) could reach 90%. Nanthi et al. [24] used sodium hydroxide (NaOH) to modify adsorbents and then used the as-modified adsorbents to treat Pb (II)-polluted water, and the removal rate reached 90%. Moreover, some researchers also found that calcination could also improve the adsorption capacity of adsorbents [25,26]. Efficiency of single-modified kaolin for removal of heavy metals is well documented. However, only few studies have investigated the adsorption capacity of kaolin modified with combination of processes such as modification with alkali followed by calcination.

The main objectives of this research included further systematic explorations and extended investigation on the abilities of natural, NaOH-modified, and NaOH-calcination-modified kaolin for the removal of Pb (II) and Cd (II) from wastewater, and application of modified kaolin obtained by combination of processes to actual industrial wastewater treatment. Characterization of the natural and modified kaolin was systematically performed. Specific parameters including contact time, calcination temperature, pH, and kaolin dosage were studied in Pb (II) and Cd II) adsorption process. Furthermore, isothermal adsorption and adsorption kinetics were evaluated to describe the adsorption mechanism for heavy metal ions on natural kaolin and modified kaolin.

2. Materials and methods

2.1. Kaolin

The natural kaolin was purchased from Yuanheng Water Purification Plant (China). It was cleaned with deionized water to remove dust, and boiled in deionized water for 2 h to eliminate the interference of microorganisms.

NaOH-modified kaolin was obtained via water bath heating with NaOH solution (3.0 mol L^{-1}) at 70°C for 7 h. Then kaolin was washed with deionized water to neutralize it. After drying at 105°C for 5 h, NaOH-modified kaolin was ground and stored in dryer.

NaOH-calcination-modified kaolin was obtained by calcination of NaOH-modified kaolin for 3 h at 200, 300, 400, 500, and 600°C, respectively. The combined modified kaolin was cooled and washed with deionized water. After drying at 105°C for 5 h, NaOH-calcination-modified kaolin was ground and stored in dryer.

2.2. Chemicals

Lead nitrate ($Pb(NO_3)_2$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), and NaOH were purchased from Sinopharm (China). All chemicals were of analytical grade. Aqueous solutions of all heavy metal ions were prepared using deionized water.

2.3. Industrial wastewater

Actual wastewater sample was collected from local printing plant. Initial Pb (II) and Cd (II) concentration of industrial wastewater was 201.35 and 200.15 mg L^{-1}, respectively, and the pH of wastewater was 5.8.

2.4. Analysis

Concentration of heavy metal ions was measured by using a flame-graphite furnace atomic absorption spectrophotometer (ZEEnit700P, Analytik Jena AG). Scanning electron microscopy (SEM, JSM-5610LV, JEOL) was performed to characterize the samples. Fourier transform infrared (FTIR) spectrum was obtained using a Nicolet 6700 (Thermo Fisher Scientific) FTIR spectrometer. Autosorb-1 (Quantachrome Instruments) automatic specific surface area (SSA) and pore size distribution analyzer were used to determine SSA.

2.5. Adsorption experiments

Batch adsorption experiments were conducted by mixing kaolin with 100 mL solution of required concentration in 150 mL flask. Flask was shaken at 180 rpm at room temperature (25°C) for different time (5–2880 min). The pH was changed from 4 to 8, and it was adjusted by using 0.5 M HCl or NaOH solution. Supernatant was collected in 20 mL centrifuge tube, and centrifuged at 2000 rpm for 10 min. Supernatant was refrigerated prior to determination.

The effects of parameters such as calcination temperature, contact time, adsorption temperature, initial pH, and kaolin dosage were investigated in these experiments. The removal rate (R%) was calculated by using the following equation:

$$R = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

The adsorption capacity (q_e, mg g^{-1}) was calculated by using following equation:

$$q_e = \frac{(C_o - C_e)}{C_o} V \tag{2}$$

where C_0 and C_e are, respectively, the initial and equilibrium concentrations of heavy metal ions (mg L^{-1}), V is the volume of solution (L), and m is the amount of adsorbent (g).

2.6. Adsorption isotherms and kinetics

Langmuir and Freundlich isotherm models [27] were adopted for analyzing the isothermal adsorption process and its corresponding parameters.

Langmuir adsorption isotherm:

$$\frac{C_e}{Q} = \frac{1}{Q_m} \cdot K_a + \frac{C_e}{Q_m} \tag{3}$$

Freundlich adsorption isotherm:

$$\lg Q = \lg K_f + \frac{l}{n} \lg C_e \tag{4}$$

where C_e is adsorption equilibrium concentration of adsorbate (mg L^{-1}), Q is adsorption equilibrium quantity (mg g^{-1}), Q_m is adsorption capacity, K_a is Langmuir constant, K_f is Freundlich constant, and *n is* constant representing adsorption strength.

In this study, Lagergren pseudo-first order reaction kinetics equation and pseudo-second order reaction kinetics equation were adopted [28]. Elovich equation and particle diffusion rate equation [29] were used in this study.

Pseudo-first order reaction kinetics equation:

$$\lg\left(q_e - q_t\right) = \lg q_e + \frac{K_1}{2.303} \cdot t \tag{5}$$

Pseudo-second order reaction kinetics equation:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^{\,2}} + \frac{t}{q_e} \tag{6}$$

Elovich equation:

$$q_t = C_1 + K_3 \ln t \tag{7}$$

Particle diffusion rate equation:

$$q_t = C_2 + K_4 t^{0.5} \tag{8}$$

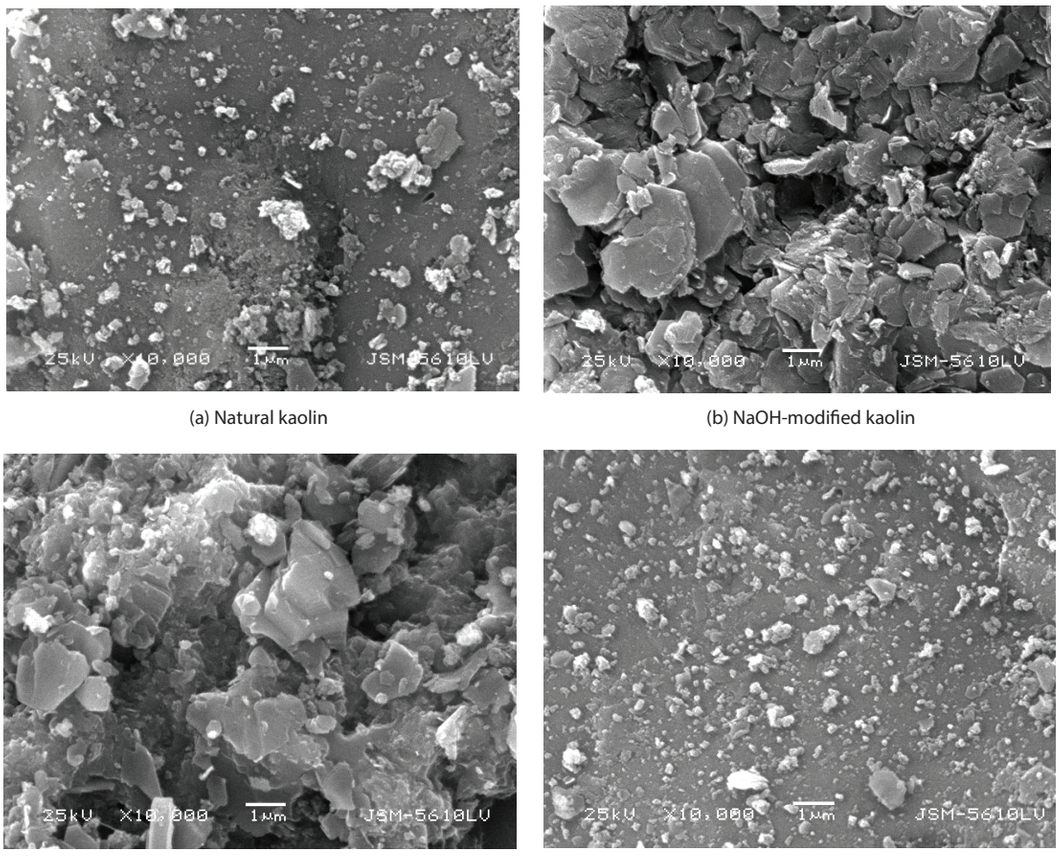
where q_t is adsorption capacity at adsorption time t (mg g^{-1}), q_e is adsorption equilibrium capacity (mg g^{-1}), k_1 and k_2 are pseudo-first and pseudo-second order adsorption rate constants, respectively, k_3 is Elovich adsorption rate constant, k_4 is particle diffusion adsorption rate constant, and c_1 and c_2 are constants.

3. Results and discussion

3.1. Characterization of modified kaolin

3.1.1. Scanning electron microscopy analysis

Fig. 1a shows that natural kaolin has dense structure and its surface has small inhomogeneous pores. Fig. 1b exhibits the obvious layer structure of NaOH-modified kaolin with coarse and loose surface, which led to the increase in the SSA of kaolin, thus the adsorption capacity of kaolin could be increased. The shape of combined modified kaolin (calcined at 400°C) was irregular and the structure of kaolin surface was loose with bigger pore volume (Fig. 1c), which could increase the possibility of trapping heavy metal ions for kaolin. Fig. 1d shows the collapsed surface of combined modified kaolin (calcined at 500°C) because of the structural damaged which occurred at higher temperature.



(a) Natural kaolin

(b) NaOH-modified kaolin

(c) NaOH-calcination-modifiedkaolin(400°C)

(d) NaOH-calcination-modified kaolin(500°C)

Fig. 1. SEM images of four types of kaolin.

3.1.2. Fourier transform infrared spectroscopy analysis

FTIR spectra of natural kaolin, NaOH-modified kaolin, and NaOH-calcination-modified kaolin are shown in Fig. 2. The absorption peaks of bound water are observed at around 1637 and 3448 cm^{-1}, and the figures for natural kaolin and NaOH-modified kaolin do not exhibit significant change. The absorption peaks at 1637 and 3448 cm^{-1} exhibit a weakening trend after high temperature calcination. This indicates that high temperature calcination led to the dehydration of kaolin, which improved its adsorption capacity.

3.1.3. Specific surface area analysis

Barrett–Emmett–Teller (BET) method was used to measure SSA [30]. The SSA of natural, NaOH-modified, and combined modified kaolin was found in the following sequence: combined modified kaolin (21.2820 m^2 g^{-1}) > NaOH-modified kaolin (9.1710 m^2 g^{-1}) > natural kaolin (4.3010 m^2 g^{-1}) (Table 1). Moreover, it was also observed that combined modified kaolin exhibited the largest pore volume among the three types of kaolin, and this clearly indicated that the pore volume was relevant to SSA change for modified kaolin.

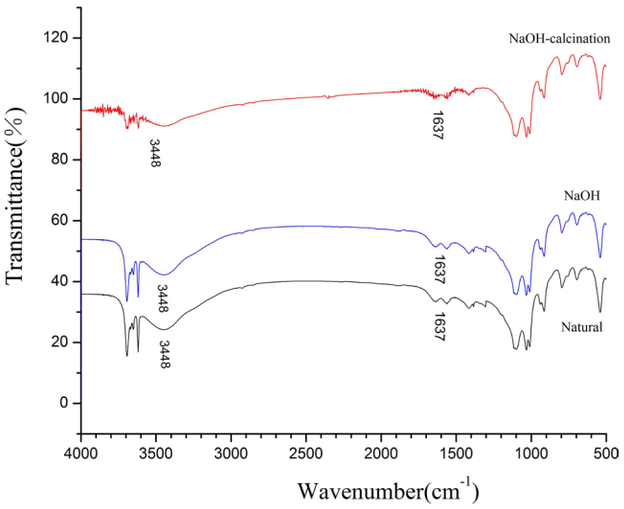


Fig. 2. FTIR spectra for natural kaolin, NaOH-modified kaolin, and NaOH-calcination-modified kaolin.

Table 1
SSA and pore size of kaolin samples

Type of modified kaolin	Natural kaolin	NaOH-modified kaolin	NaOH-calcination-modified kaolin
SSA (m^2 g^{-1})	4.3010	9.1710	21.2820
Pore volume (cm^3 g^{-1})	0.01761	0.06101	0.06987
Average pore size (nm)	175.9090	81.7947	68.3974

3.2. Studies on adsorption capacity of combined modified kaolin

3.2.1. Effect of calcination temperature

Calcination temperature is a significant factor for kaolin modification process. When heavy metal ions concentration was 200 mg L^{-1}, adsorption temperature was 25°C, contact time was 60 min, kaolin dosage was 1 g, and pH of the solution was 5.5, NaOH-modified kaolin was calcined at different temperatures, respectively. Fig. 3 shows the effect of calcination temperature on removal of Pb (II) and Cd (II). Clearly, the removal rate of Pb (II) and Cd (II) increases with the increase in the calcination temperature from 200 to 400°C. At 400°C, the maximum removal rates of Pb (II) and Cd (II) were 80.92 and 50.51%, respectively. However, when the temperature was kept on increasing, the removal rate of Pb (II) and Cd (II) reduced. The pores structure of modified kaolin collapsed due to high temperature calcination, as demonstrated by SEM images shown in Figs. 1c and 1d. Thus, the adsorption capacity was enhanced significantly with calcination of NaOH-modified kaolin at a suitable temperature of 400°C.

3.2.2. Effect of contact time

The influence of contact time on Pb (II) and Cd (II) retention onto natural kaolin, NaOH-modified kaolin, and NaOH-calcination-modified kaolin was studied as presented in Fig. 4. The contact time was varied in the range of 0–2880 min, the initial heavy metal ions concentration was 200 mg L^{-1}, and pH of the solution was 5.5. Adsorption temperature was 25°C and kaolin dosage was 1 g. Fig. 4 demonstrates that the removal rate of Pb (II) exhibits a steady increase for the first 40 min, followed by an appreciable stabilization trend from about 60 min for natural kaolin, about 90 min for NaOH-modified kaolin, and about 120 min for combined modified kaolin. However, the removal rate of Cd (II) treated with combined modified kaolin increases in the first 60 min, and then approaches equilibrium. The curve of Cd (II) removal on NaOH-modified and natural kaolin becomes steady after contacting time of 40 min. Fig. 4 clearly shows that combined modified kaolin is a quicker and efficient adsorbent for Pb (II) and Cd (II) than NaOH-modified and natural kaolin. In the first 60 min, the adsorption progress of heavy metal ions was completed by around 90%; therefore, 60 min was selected as the optimized contact time in the follow-up experiments assuming that the adsorption progress was entirely completed.

3.2.3. Effect of adsorption temperature

Furthermore, the effect of adsorption temperature was evaluated and discussed. The initial concentration of heavy metal ions was 200 mg L^{-1}. Adsorption temperature was set from 20 to 40°C, pH of the solution was 5.5, contact time was 60 min, and kaolin dosage was 1 g. Fig. 5 shows that the combined modified kaolin exhibits the best adsorption capacity, and with the increase in the temperature the removal rate of Pb (II) shows little change, while Cd (II) removal rate increases slightly. This might be attributed to the fact that the Cd (II) activity was sensitive to temperature, and high temperature accelerated the adsorption of

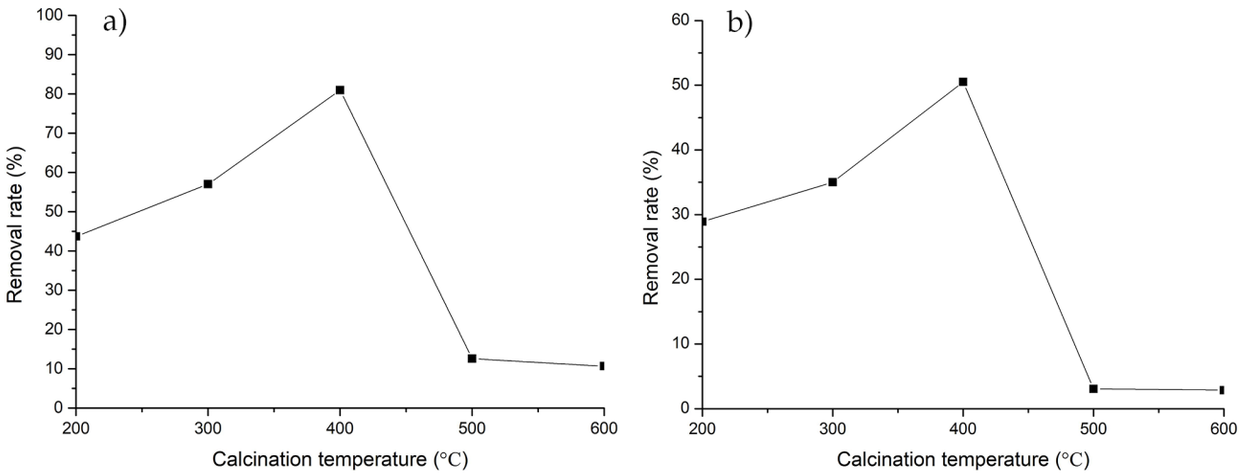


Fig. 3. (a) The effect of calcination temperature on the removal of Pb (II) and (b) The effect of calcination temperature on the removal of Cd (II).

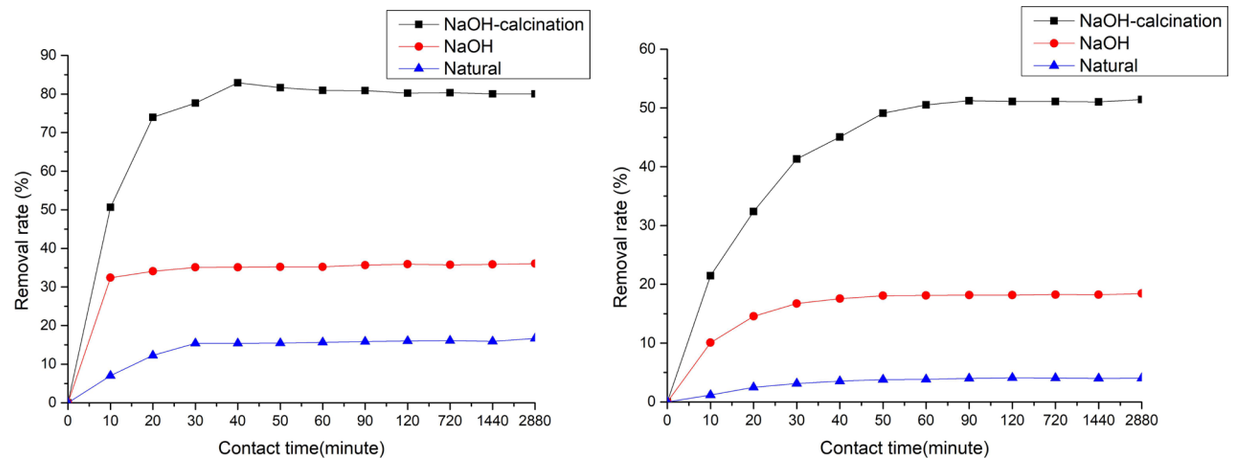


Fig. 4 (a) The effect of contact time on the removal of Pb (II) and (b) The effect of contact time on the removal of Cd (II).

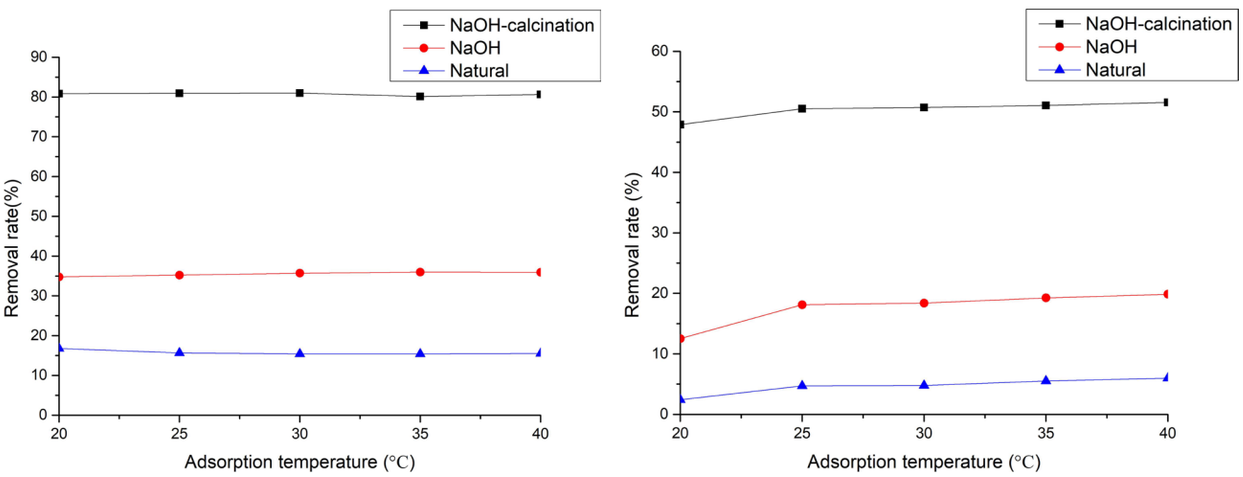


Fig. 5 (a). The effect of adsorption temperature on the removal of Pb (II) and (b) The effect of adsorption temperature on the removal of Cd (II).

Cd (II). In further experiments, adsorption temperature was set at room temperature (25°C).

3.2.4. Effect of pH

The pH of solution is an important factor significantly influencing the heavy metal ions removal in adsorption process [31,32]. The effect of pH on Pb (II) and Cd (II) removal is shown in Fig. 6. Kaolin dosage was 1 g and initial concentration of heavy metal ions was 200 mg L^{-1}. Adsorption temperature was 25°C and contact time was 60 min. The adsorption capacity of three types of kaolin was found to be pH dependent, and all of them showed a weak adsorbing ability when pH was low. With the increase in the pH of aqueous solution to around 8, the removal rate of Pb(II) on NaOH-modified and combined modified kaolin could reach 99.48 and 99.99%, respectively, while the removal rate on natural kaolin was 70.61%. The maximum removal rate of Cd (II) on combined modified kaolin was 99.97% at pH 8. At low pH, protons would compete fiercely with heavy metal ions for adsorption sites in solution, resulting in low removal efficiency of heavy metal ions. With the increase in the pH, linked H^+ ions were released from the active sites, and the amount of adsorbed heavy metal ions increased [33,34]. However, when the initial pH of the solution was greater than 6.0, heavy metal ions were precipitated due to higher concentration of OH^- in the solution [35]. Thus, the pH of the experiment was adjusted to 5.5.

3.2.5. Effect of kaolin dosage

The effect of kaolin dosage on the removal of heavy metal ions with the initial concentration of 200 mg L^{-1} is illustrated in Fig. 7. Adsorption temperature was 25°C, pH of the solution was 5.5, contact time was 60 min, and the dosage of kaolin ranged from 1 to 3 g. Notably, the absorption capacity of combined modified kaolin was found to be better than that of natural and NaOH-modified kaolin. Adsorption capacity of heavy metal ions on combined modified kaolin decreased with the increase of kaolin dosage. The maximum adsorption capacity of heavy metal ions were 161.84 and 108.13 mg g^{-1}, respectively, when the kaolin dosage was 1 g. For NaOH-modified kaolin, the heavy metal ions adsorption capacity increased when the dosage

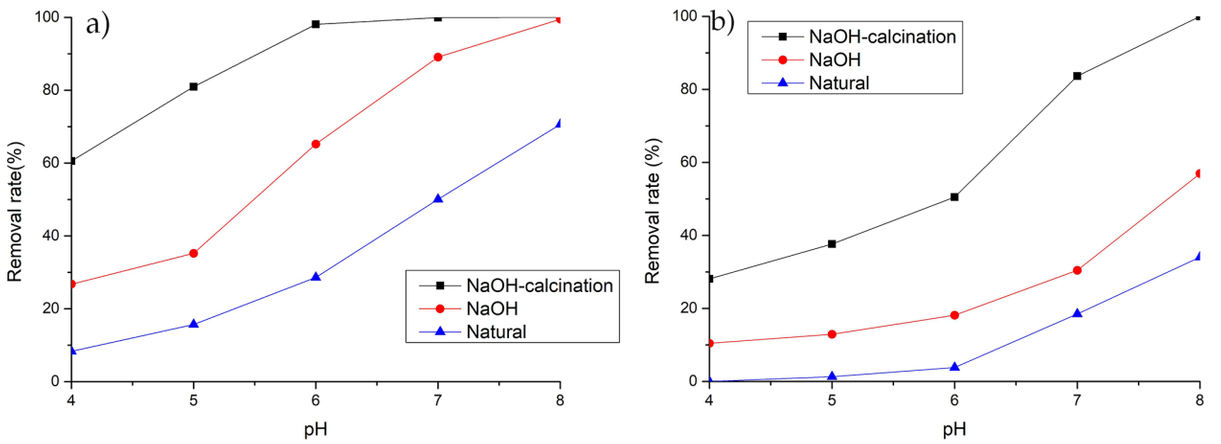


Fig. 6 (a). The effect of pH on the removal of Pb (II) and (b) The effect of pH on the removal of Cd (II).

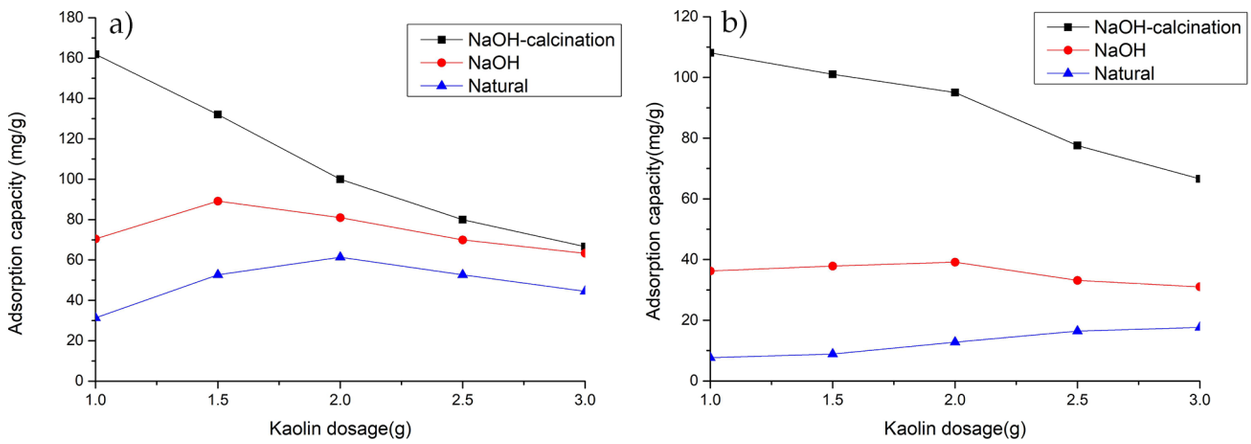


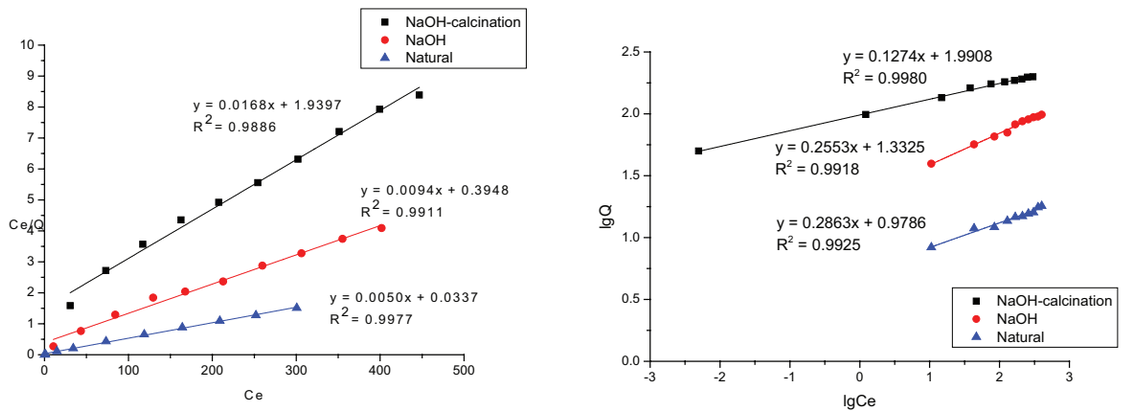
Fig. 7 (a). The effect of kaolin dosage on the adsorption of Pb (II) and (b) The effect of kaolin dosage on the adsorption of Cd (II).

of kaolin was less than 1.5 and 2.0 g, respectively, and then the adsorption capacity decreased. When kaolin reached adsorption saturation state, the adsorption sites would be added with the increase in the kaolin dosage; however, heavy metal ions concentration was fixed, and the amount of heavy metal ion adsorbed on unit kaolin would reduce. On the other hand, the large amount of kaolin led to aggregation of kaolin particles, thus resulting in reduction in the specific surface of kaolin [36].

3.2.6. Adsorption isotherm

The relationship between adsorbent and adsorbate can be accurately evaluated by using adsorption isotherm models [31]. Langmuir and Freundlich isotherm models were exploited to study the adsorption process of heavy metal ions on kaolin. In this study, the adsorption process of Pb (II) (Fig. 8) was presented as an example due to its higher removal rate. The parameters for isotherm were calculated and listed in Table 2. The results showed that the correlation coefficient value of Langmuir isotherm for Pb (II) (R^2 = 0.9977) was nearly similar to that of Freundlich isotherm (R^2 = 0.9980), which indicated that both Langmuir and Freundlich models could characterize the adsorption process appropriately. According to Freundlich model, the value of 1/n ranged from 0.1 to 0.5, which indicated easy occurrence of the adsorption process [37].

Langmuir adsorption capacities of Pb(II) on three different types of kaolin were compared with those of various low cost adsorbents as summarized in Table 3. The sorption capacity by various sorbents exhibited variation due to difference in physico-chemical properties of adsorbents and experimental factors including the concentration range of pollutants (Pb), pH, temperature, etc. [38]. Langmuir sorption capacity of investigated heavy metal ions by kaolin was found to be significantly higher than that of low cost



(a) Langmuir isotherms equation

(b) Freundlich isotherms equation

Fig. 8. The isotherms curves for the adsorption of three types of kaolin.

Table 2
Langmuir and Freundlich isotherms parameters for Pb(II) adsorption

Type of modified kaolin	Langmuir model			Freundlich model		
	Q_m (mg g^{-1})	k^a	R^2	K^f	$1/n$	R^2
NaOH-calcination-modified kaolin	200	0.1484	0.9977	97.9039	0.1274	0.9980
NaOH-modified kaolin	106.383	0.0238	0.9911	21.5030	0.2553	0.9918
Natural kaolin	59.5238	0.0087	0.9886	9.5192	0.2863	0.9925

Table 3
Comparison of Langmuir sorption capacity for Pb(II) with various low cost adsorbents

Adsorbent	Adsorption capacity of metal ion (mg g^{-1})	Condition	Reference
	Pb		
Sericite	4.7	pH 5.5–5.8, 25 °C	[39]
Bentonite	32.68	pH 5, 25 °C	[40]
Scolecite	5.8	pH 6, 25 °C	[41]
Natural kaolin	59.52	pH 5.5, 25 °C	Present study
NaOH-calcination-modified kaolin	200	pH 5.5, 25 °C	Present study

adsorbents. After modifying kaolin by NaOH and calcination, the Langmuir sorption capacity of Pb showed an obvious increase compared to natural kaolin, which is about 3.33 times higher than that of natural kaolin.

3.2.7. Adsorption kinetics

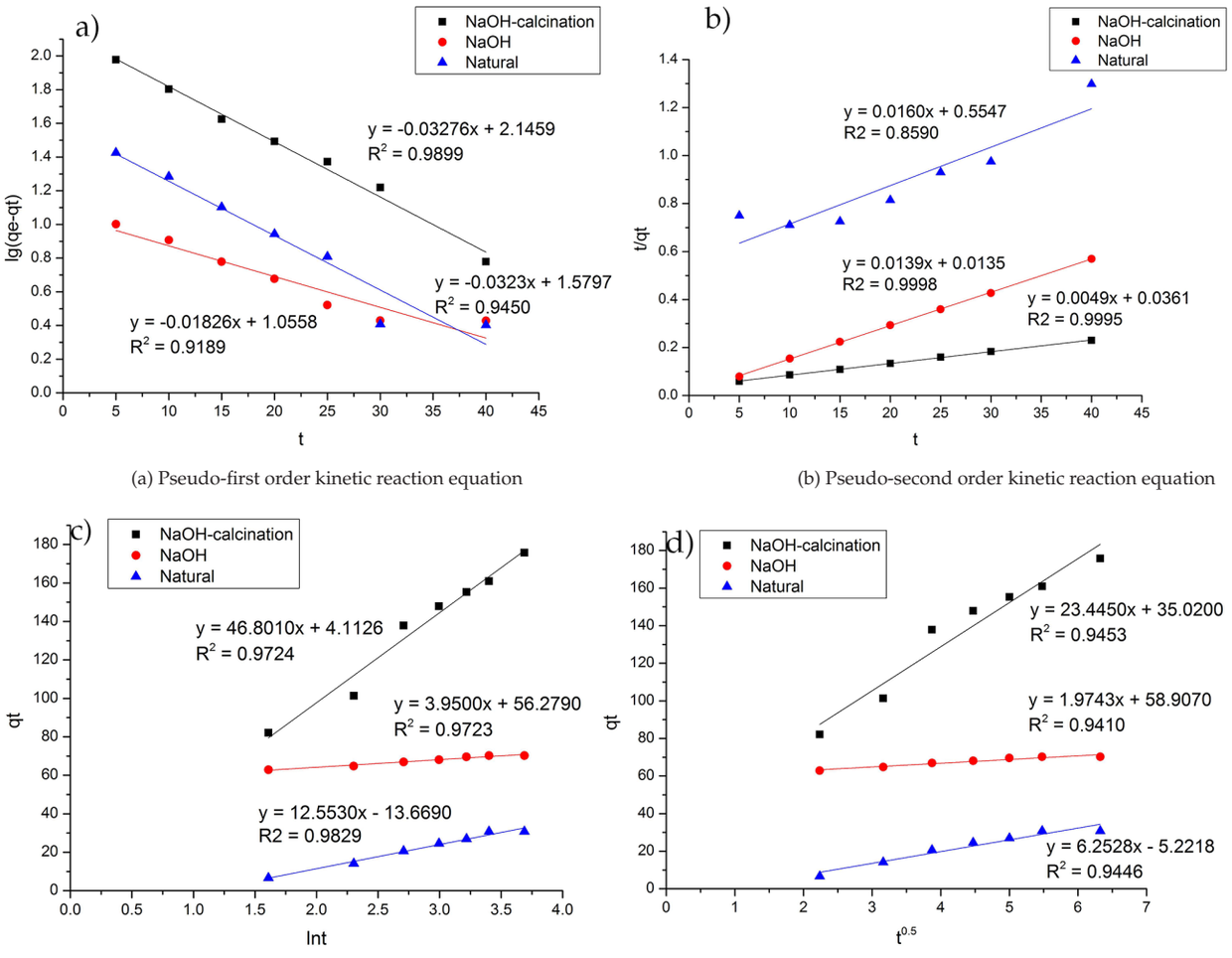
In this study, the adsorption kinetics of Pb (II) was discussed. Four adsorption kinetic models were used to discuss the adsorption kinetics of Pb (II) on kaolin. The adsorption kinetic curves of modified kaolin are shown in Fig. 9. Clearly, pseudo-second order reaction kinetics equation better fits the adsorption process of modified kaolin, which indicates that chemical adsorption plays a main role in this process [36]. The results illustrated that the correlation coefficient value of Elovich kinetic equation was 0.9724 for Pb (II), which revealed that the adsorption process of Pb (II) on modified kaolin was heterogeneous adsorption. Moreover, the correlation coefficient value of particle diffusion model was 0.9453 for Pb (II), which indicated that the adsorption process of modified kaolin for heavy metal ions was not controlled by just particle diffusion.

3.3. Application of combined modified kaolin on industrial wastewater treatment

NaOH-calcination-modified kaolin exhibited the best adsorption capacity among the three different types of kaolin as shown above. Natural and combined modified kaolin were applied to treat industrial wastewater. The initial concentrations of Pb (II) and Cd (II) of actual wastewater were 201.35 and 200.15 mg L^{-1}, respectively, and the pH of wastewater was 5.8.

3.3.1. Effect of contact time

The influence of contact time on the removal of heavy metal ions from actual wastewater samples on natural and combined modified kaolin was investigated. The contact time was set from 0 to 2880 min and kaolin dosage was 1 g. Fig. 10 depicts that removal rate of Pb(II) increases rapidly in the first 30 min, followed by an appreciable stabilization trend from about 30 min for the combined modified kaolin and about 40 min for natural kaolin. The removal rate of Pb (II) on combined kaolin reaches to 84.38% at 30 min,



(a) Pseudo-first order kinetic reaction equation

(b) Pseudo-second order kinetic reaction equation

(c) Elovich kinetic equation

(d) Particle diffusion model

Fig. 9. The adsorption kinetics curves for the adsorption of three types of kaolin.

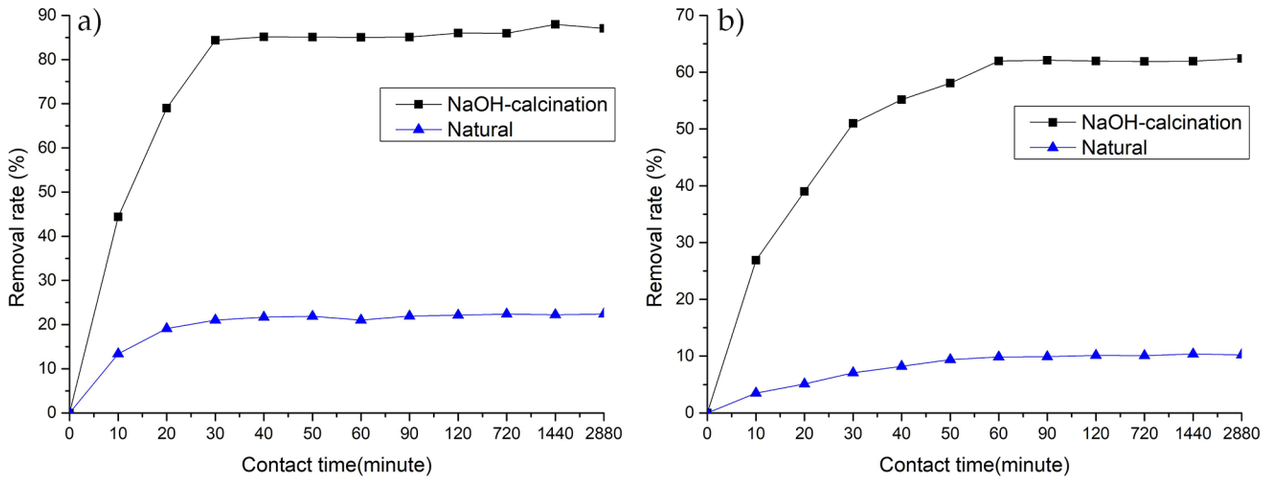


Fig. 10. (a) The effect of contact time on the removal of Pb(II) and (b) The effect of contact time on the removal of Cd(II).

while the value of natural kaolin is only 21.04%. Removal rate of Cd (II) could reach the maximum at 60 min, which was about 62% on combined modified kaolin and about 10% on natural kaolin. Clearly, the combined modified kaolin acted as a quicker and efficient adsorbent of heavy metal ions from wastewater than natural kaolin.

3.3.2. Effect of kaolin dosage

The dosage of kaolin ranged from 1 to 3 g and contact time was 60 min. Fig. 11 demonstrates that the adsorption capacity of combined modified kaolin and natural kaolin toward Pb (II) reach the maximum at the kaolin dosage of 1.0 and 2.5 g, respectively, which are 168.77 and 48.79 mg g^{-1}. With the increase in the dosage of combined modified kaolin, Pb (II) removal rate increased and reached the maximum of 99.89% when kaolin dosage was 1.5 g. However, when kaolin dosage was 1.0 g, Pb (II) adsorption capacity of combined modified kaolin was the highest and Pb (II) removal rate could also reach up to 84.38%, thus the dosage of 1 g was more economical in the treatment of actual Pb (II) containing wastewater. When kaolin dosage was 2 g, adsorption capacity of Cd (II) on combined modified kaolin could reach the maximum of 98.99 mg g^{-1}, and Cd (II) removal rate was 98.99%. Thus, the dosage of 2 g of combined modified kaolin was recommended to treat Cd (II) wastewater.

3.3.3. Adsorption kinetics

In this study, the adsorption kinetics of Pb (II) on two kaolins were discussed. Table 4 summarizes that pseudo-second order reaction kinetics equation better fits the adsorption process of modified kaolin, which indicates that chemical adsorption plays a main role in this process [36]. The results also illustrated that the correlation coefficient value of Elovich kinetic equation was 0.9819, which revealed that adsorption process of Pb (II) on modified kaolin was heterogeneous adsorption. Furthermore, the correlation coefficient value of particle diffusion model was 0.9614, which indicated that the adsorption process of modified kaolin for Pb (II) was not controlled by just particle diffusion.

4. Conclusion

In this research, natural, NaOH-modified, and NaOH-calcination-modified kaolin were investigated for the removal of Pb(II) and Cd(II) from wastewater. The adsorption capacity of these modified kaolin for Pb(II) and Cd(II) followed this order: NaOH-calcination-modified kaolin > NaOH-modified kaolin > natural kaolin. The shape of combined modified kaolin was irregular and its surface was rough and loose with bigger pore volume. The adsorption capacity of Pb(II) and Cd(II) could reach the maximum of 161.84 and 108.13 mg g^{-1}, respectively, under the following experimental conditions: initial concentration of heavy metal ions was 200 mg L^{-1}, pH was 5.5, adsorption temperature was 25°C, contact time was 60 min, and NaOH-calcination-modified kaolin dosage was 1 g. The adsorption temperature exhibited little influence on heavy metal ions removal; however, pH of the solution could significantly affect the removal rate of heavy metal ions. Furthermore, Langmuir isotherm model and Freundlich isotherm model could well fit heavy metal ions adsorption isotherm, demonstrating that both the models could characterize the adsorption process appropriately. The pseudo-second order model could well fit with the experimental data to indicate the adsorption kinetics of heavy metal ions on the combined modified kaolin. Moreover, the Elovich kinetic equation indicated that the adsorption process of heavy metal ions on kaolin was heterogeneous adsorption. Combined modified kaolin was also applied to treat actual industrial wastewater samples and showed effective removal of Pb (II) and Cd (II) from actual wastewater. The results clearly indicate that NaOH-calcination-modified kaolin is supposed to be an efficient adsorbent for the removal of heavy metal ions from wastewater.

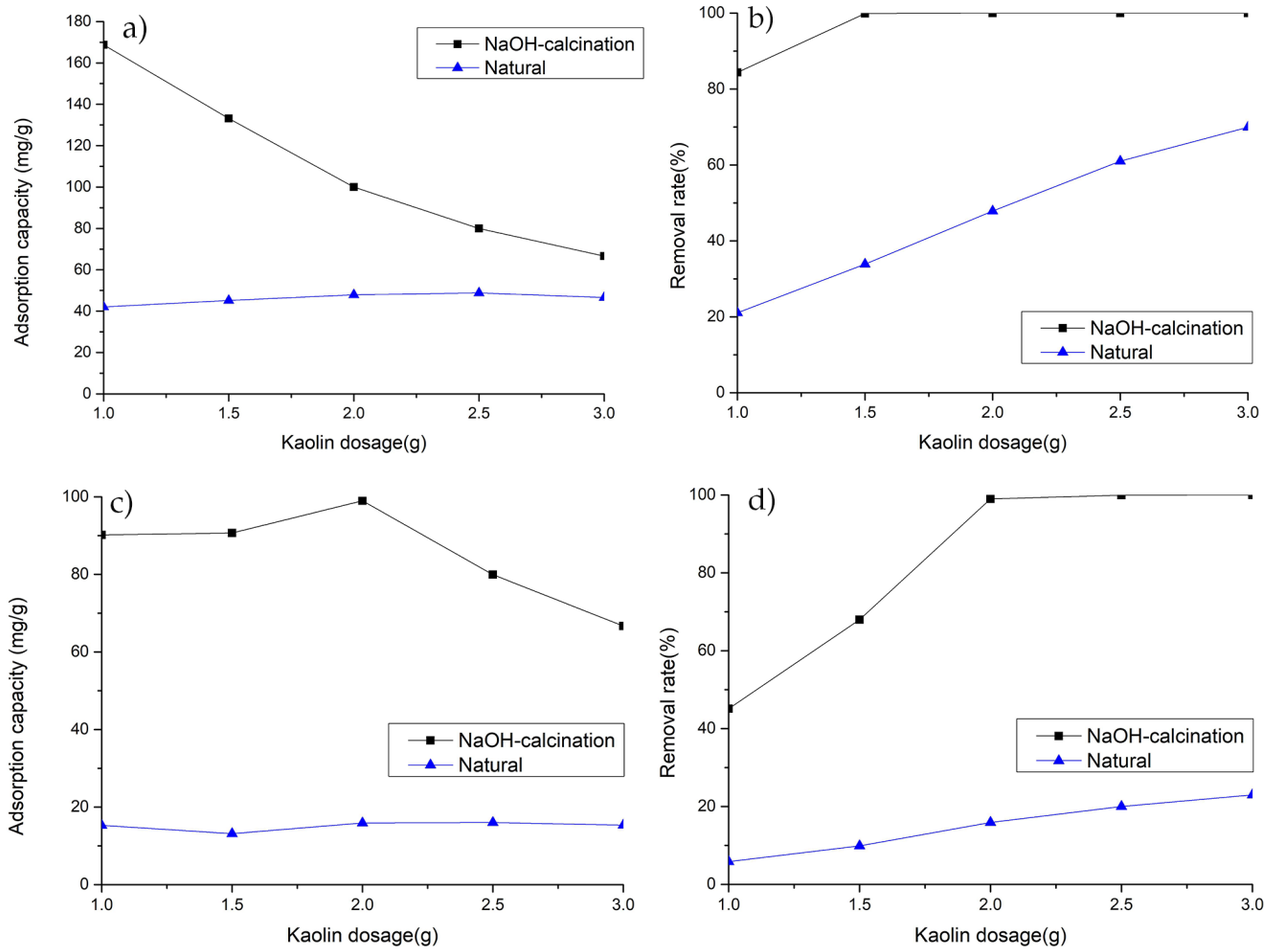


Fig. 11 (a) and (b) the effect of kaolin dosage on the adsorption of Pb(II) and (c) and (d) the effect of kaolin dosage on the adsorption of Cd(II).

Table 4
The parameters of adsorption kinitics for Pb(II) adsorption of two kaolin

Type of kaolin	Actual adsorption capacity	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		q_e^1	K_1	R^2	q_e^2	K_2	R^2
Combined modified kaolin	175.98	224.18	0.0977	0.9598	210.084	0.0003	0.9868
	44.419	43.803	0.0965	0.9972	55.5556	0.0018	0.9958
Type of kaolin	Elovich model			Particle diffusion model			
	K_3	C_1	R^2	K_4	C_2	R^2	
Combined modified kaolin	59.241	–41.25	0.9819	29.343	–1.1117	0.9614	
Natural kaolin	12.937	–2.2649	0.9799	6.2892	7.0405	0.9242	

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