



Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay

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ABSTRACT

Modified kaolinite clay with 25% (w/w) aluminium sulphate and unmodified kaolin were investigated as adsorbents to remove Pb(II) from aqueous solution. The results show that amount of Pb(II) adsorbed onto modified kaolin (20 mg/g) was more than 4.5-fold than that adsorbed onto unmodified kaolin (4.2 mg/g) under the optimized condition. In addition, the linear Langmuir and Freundlich models were used to describe equilibrium isotherm. It is observed that the data from both adsorbents fitted well to the Langmuir isotherm. The kinetic adsorption of modified and unmodified kaolinite clay fitted well to the pseudo-second-order model. Furthermore, both modified and unmodified kaolinite clay were characterized by X-ray diffraction, Fourier transform infrared (FT-IR) and scanning electron microscope (SEM). Finally, both modified and unmodified kaolinite clay were used to remove metal ions from real wastewater, and results show that higher amount of Pb(II) (the concentration reduced from 178 to 27.5 mg/L) and other metal ions were removed by modified kaolinite clay compared with using unmodified adsorbent (the concentration reduced from 178 to 168 mg/L).

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1. Introduction

As one of the important pollutants in wastewater, heavy metal becomes a severe public health problem because of its non-biodegradable and persistent nature. Lead is an important metal from the viewpoint of environmental toxicology as the metal finds its way into air and water from a multitude of sources like lead smelter, battery manufacturer, paper and pulp industry, boat and ship fuel and ammunition industry [1,2]. Several methods have been used for its removal from aqueous solutions, including chemical precipitation, ion exchange, solvent extraction, ultrafiltration, reverse osmosis, electrodialysis, and adsorption [3]. However, due to the high maintenance costs and some other factors, such as the presence of pollutants in trace amounts and a large amount of sludge for chemical precipitation, most of these methods are unsustainable in developing countries. In contrast, adsorption of Pb(II) from aqueous solution have been investigated by using various adsorbents [4–7]. Among them, natural clays as low-cost adsorbents, have received much attention in heavy metals sorption from contaminated water due to their acceptability and applicability.

Kaolin is one of the plentiful natural clays in China, and it is a 1:1 clay mineral with the ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [8]. A number of studies concerning kaolinite clay used to remove heavy

metals such as Fe(III), Co(II) and Ni(II) from aqueous solution have been reported [9–13]. The removal of metal ions using kaolinite clay is based on ion exchange and adsorption mechanisms as it has a low cation exchange capacity (CEC) (15–75 mmol/kg of clay) and small surface area commonly ranging from 10 to 20 m²/g [10]. The saturated amount (Q_0) of Cd(II) adsorbed by kaolin was found to be only 13.03 mmol/kg [14], and 11.2, 11.0, 10.4 mg/g of Fe(III), Co(II) and Ni(II) retained on kaolin was found, respectively [11]. However, clay can be modified to improve its sorption capacity. Intercalation, pillaring, and other chemical modifications are the common techniques [12]. Clays pillared with metal oxides are of great importance because of their high thermal stability, high surface area, and intrinsic catalytic activity [12]. Numerous cations (hydroxyl aluminum and zirconium) [13], have been used for the preparation of pillared clay, which have a high sorption capacity of heavy metals at adequate pH. As an alternative technique, chemically modified clay minerals represent a new class of adsorbents for water purification and industrial wastewater treatment [14]. Kaolinite clay has also been modified with orthophosphate, tri-polyphosphate or sulphate [15–17]. 2-mercapto-benzothiazole impregnated clay surface, surfactant and ZrO-modified kaolins have also been used for the removal of some heavy metal ions from water samples [18–20].

In this study, the feasibility of using modified and unmodified kaolin as adsorbents for the removal of Pb(II) from aqueous solution was investigated. To achieve the aim, the conditions for adsorption, including contact time, pH, initial Pb(II) concentration and

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ionic strength were required to be optimized with respect to the efficiency of Pb(II) removed. In addition, to determine whether the possibility of both modified and unmodified kaolin used to remove Pb(II) and the difference between modified and unmodified kaolin, real wastewater was tested using both kaolins. Furthermore, to understand the adsorption of Pb(II) onto modified and unmodified kaolins, the kinetic of adsorption and the evidences for physicochemical characteristics of both kaolins obtained from Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM) were presented.

2. Experimental

2.1. Materials

The kaolin sample was obtained from Kaolin Company of Longyan, Fujian. Both modified and unmodified kaolin were dried and sieved to +150 μm particle size before used as adsorbents. All chemicals used in this study were analytical reagent grade and used without further purification. The cation exchange capacity of kaolinite clay is 95 mmol/kg while the CEC of the modified kaolin is 236 mmol/kg as established by the method of ammonium chloride and ammonia. The BET surface area of both kaolinite clay and modified kaolin are 3.7 and 10.2 m^2/g , respectively.

2.2. Modification of clay sample

Kaolin samples (100 g) were mixed with $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (25 g), active carbon (2 g) and some distilled water, then mix round manually with a glass stick until being mushy. After half-hour stabilization, the mixture was dried in an oven at 100 $^\circ\text{C}$ for 1 h and then baked in the muffle oven at 420 $^\circ\text{C}$ for 2 h. Thereafter, the modified production was also sieved to +150 μm particle size.

2.3. Characterization of kaolin

The infrared spectroscopy of both modified and unmodified samples were obtained using a Fourier transform infrared (FT-IR) spectrometer (Fourier-380FT-IR, America). The crystallinity of the modified and unmodified kaolin was determined by powder X-ray diffraction (X' Pert Pro MPD, Holland) with filtered Cu $K\alpha$ radiation operated at 40 kV and 40 mA. The XRD pattern was recorded from 1.5 $^\circ$ to 50 $^\circ$ of 2θ with a scanning speed of 0.02 $^\circ$ of 2θ per second. Solid morphology and average crystal size were determined by scanning electron microscopy (SEM) (Philips-FEI XL30 ESEM-TMP, Holland).

2.4. Batch equilibration method

The adsorption of Pb(II) by modified and unmodified kaolin were studied by a batch operation, including effects of contact time, the solution pH, ionic strength and initial metal ion concentration. Distilled water was used in all experiments. Stock solutions of lead were prepared from $\text{Pb}(\text{NO}_3)_2$. Batch sorption experiments were performed at 30 $^\circ\text{C}$ under natural pH conditions with electrolyte concentration of 0.01 mol/L in a shaker incubator at 150 rpm for 1 h, using 50 mL capped plastic centrifuge tubes containing 20 mL of 500 mg/L Pb(II) solutions and 0.5 g of the adsorbents. pH of the solution was adjusted by using 0.1 mol/L HCl or NaOH and without adding any buffer to control the pH constantly, ionic strength was adjusted by using 0.1 or 0.5 mol/L NaNO_3 . After a time period of agitation, the suspensions were centrifuged at 2500 rpm for 5 min. The supernatants were then collected and analyzed for lead ions concentration by a flame atomic adsorption spectrophotometer (AA240FS, VARIAN). The effects of the following parameters to the

adsorption capacity of both modified and unmodified kaolin in the experiments were investigated.

2.5. Kinetics of Pb(II) adsorption

Stock solution of 1000 mg/L of the standardized Pb(II) was prepared from $\text{Pb}(\text{NO}_3)_2$. 250, 500 and 750 mg/L of Pb(II) solutions with 0.01 mol/L NaNO_3 were subsequently prepared. The effect of temperature on the kinetics of Pb(II) adsorbed was studied at 20, 30, and 40 $^\circ\text{C}$, some other conditions and the process of kinetic experiments were carried out as the effect of contact time with time ranges of 5–60 min.

Samples were run in duplicates. The amounts of lead ions adsorbed by the adsorbents were calculated by concentration difference using the following formula:

$$Q_t(\text{mg/g}) = \frac{(C_0 - C_t) \cdot V/1000}{W} \quad (1)$$

where Q_t is the amount of metal ion adsorbed on the adsorbent at time t , C_0 , the initial metal ion concentration (mg/L), C_t , the concentration of metal ion in solution at time t (mg/L), V , the volume of metal ion solution used (mL), and W is the weight of the adsorbent used (g).

2.6. Theory of adsorption

2.6.1. Adsorption isotherms

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most commonly used [21]. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The model takes the following form:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (2)$$

where Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and Q_0 (mg/g) and b (L/mg) are Langmuir constants.

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n (g/L) are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

2.6.2. Adsorption kinetics

The adsorption of Pb(II) onto modified and unmodified kaolin at a short time scale may involve a chemical sorption which implies the strong electrostatic interaction between the negatively charged surface and Pb(II). Y.S. Ho developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat [15]. This model has since been widely applied to a number of metal/sorbent sorption systems. The linear form of the diffusion equation is described in the following form:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \quad (4)$$

where Q_e is the amount of Pb(II) adsorbed at equilibrium (mg/g), Q_t , the amount of Pb(II) adsorbed at time t (mg/g) and k is the rate

constant of the pseudo-second-order sorption (g/mg min^{-1}). The initial sorption rate h (mg/g min^{-1}) was obtained according to Eq. (5), as t/Q_t approaches zero.

$$h = kQ_e^2 \quad (5)$$

2.6.3. Thermodynamics of adsorption

Thermodynamic parameters can be determined using the equilibrium constant, K_d (Q_e/C_e) which depends on temperature. The change in enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process were calculated by using following equations [22,23]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where R (8.3145 J/mol K) is the ideal gas constant, and T (K) is the temperature. The Gibbs free energy, ΔG° , of specific adsorption is calculated from the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

According to Eqs. (6) and (7), ΔH° , ΔS° , and ΔG° parameters can be calculated.

3. Results and discussion

3.1. Pb(II) adsorption

The adsorption trends of lead on modified and unmodified kaolin in aqueous solution were investigated as a function of contact time, pH, initial lead ion concentration and ionic strength.

3.1.1. Effect of contact time

The effect of contact time to the adsorption capacity of modified and unmodified kaolin was investigated in the time ranges of 5–120 min under natural pH at 30°C . It was observed that initial adsorption of Pb(II) was rapid on both modified and unmodified kaolin, Pb(II)–clay interactions reached equilibrium in less than 20 min (Fig. 4). Thus, the contact time of 60 min was used in the following sections. The adsorption sites on the clay minerals were quickly covered by the Pb(II) and the adsorption rate became dependent on the rate at which the metal ions were transported from the bulk liquid phase to the actual adsorption sites [11]. However, unlike the unmodified adsorbents, there was a sharp increase in the adsorption of Pb(II) on the modified sample. Clearly, modified kaolin significantly enhanced the adsorption of Pb(II), for example, the Pb(II) adsorbed by natural kaolin was less than 4 mg/g, while the amount adsorbed by modified kaolin was nearly 19 mg/g, the later is almost five times as much as the former. It indicated that the adsorption sites on the clay minerals were largely increased by modification. In addition, with the aluminium sulphate as accelerant, the ion exchange capacities of modified kaolin also improved several fold compared with the unmodified samples.

3.1.2. Effect of pH

The effect of pH on Pb(II) removal was investigated in the pH ranges of 1–6 at 30°C for 1 h as shown in Fig. 1. The aqueous solution pH is an important operational parameter in the adsorption process because of its effect on the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [24]. It can be observed that the highest adsorption of Pb(II) with modified kaolin was obtained at final $\text{pH} > 4$. With the pH increased from 4.4 to 5.8, the Pb(II) adsorbed increased from 17.7 to 18.7 mg/g, while the highest adsorption with natural kaolin was obtained at final $\text{pH} > 6$, when pH increased from 4.7 to 6.4, the

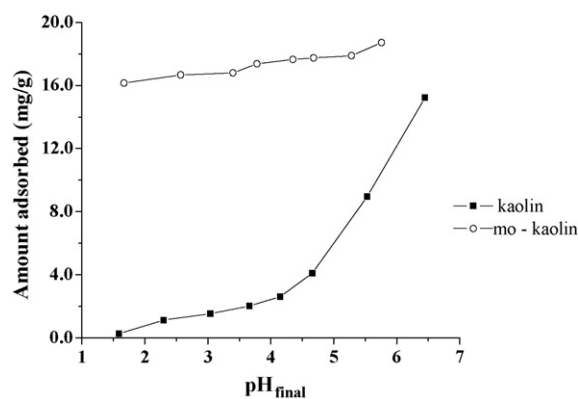


Fig. 1. Effect of pH on the adsorption of Pb(II) by the adsorbents. Initial concentration: 500 mg/L; contact time: 1 h; agitation speed: 150 rpm; dose of each adsorbent: 25 g/L; ionic strength: 0.01 mol/L; temperature of solution: 30°C .

Pb(II) adsorbed increased from 4.1 to 15.2 mg/g. In general, adsorption of Pb(II) by modified kaolin was affected less than that on natural kaolin, when the solution pH varied from 1.0 to 6.0 the adsorption of Pb(II) increased from 16.2 to 18.7 mg/g and 0.3 to 15.2 mg/g for modified and natural kaolin, respectively. The results indicated that the solution pH remarkably impacted on the adsorption of Pb(II) onto the unmodified kaolin than that of the modified kaolin. The variations in amount of Pb(II) adsorbed with pH could be explained on the basis of competition between the Pb(II) and H_3O^+ ions for adsorption sites on clay surface [1]. At low pH, the number of H_3O^+ ions exceeds that of the Pb(II) several times and the surface is most likely covered with H_3O^+ ions, which account for less Pb(II) adsorbed. When pH increases, more and more H_3O^+ ions leave the clay surface making the sites available to the Pb(II), which now increasingly bind to clay surface through a mechanism similar to that of exchange interactions (H(I)/Pb(II)). As the pH approached to a certain value, precipitation of the insoluble metal-hydroxides may appear as apparently higher metal ion removal. This can explain why Pb(II) adsorbed by natural kaolin reached 15.2 mg/g when pH was 6.4, because it is a result of adsorption and co-deposition. In addition, the point of zero charge (pH_{PZC}) of kaolin is important. When the $\text{pH} > \text{pH}_{\text{PZC}}$, adsorption of cation is favoured, while the adsorption of anions is favoured at $\text{pH} < \text{pH}_{\text{PZC}}$ [25,26]. This is why there is a significant increase in adsorption by natural kaolin at $\text{pH} > 4$.

3.1.3. Effect of ionic strength

The ionic strengths of 0.01, 0.05 and 0.1 mol/L NaNO_3 were used to test their effects on Pb(II) adsorbed by modified and unmodified kaolin at various initial Pb(II) concentrations. As shown in Fig. 2, the adsorption amount of Pb(II) onto modified and unmodified kaolin decreased with increases in the concentration of electrolyte. For example, when the concentration of NaNO_3 varied from 0.01 to 0.1 mol/L, the adsorption of Pb(II) onto unmodified kaolin and modified kaolin was reduced from 4.2 to 2.4 mg/g and 22.5 to 14.2 mg/g, respectively. However, the decrease in the maximum adsorption of Pb(II) onto unmodified kaolin was more obvious than that of the modified kaolin, the difference between modified and unmodified kaolin could be attributed to the larger surface area and stronger cation exchange capacity of the modified kaolin. The ionic strength dependence of metal ion's removal from solution by clay minerals is used to distinguish between non-specific and specific adsorption. Hence, it is concluded that the adsorption of Pb(II) by kaolin mainly proceeds through outer-sphere adsorption and inner-sphere complexation [27]. This phenomenon can be attributed to two factors [28]. First, the Pb(II) form electrical double layer complexes with the adsorbents, which favour the adsorption when the concen-

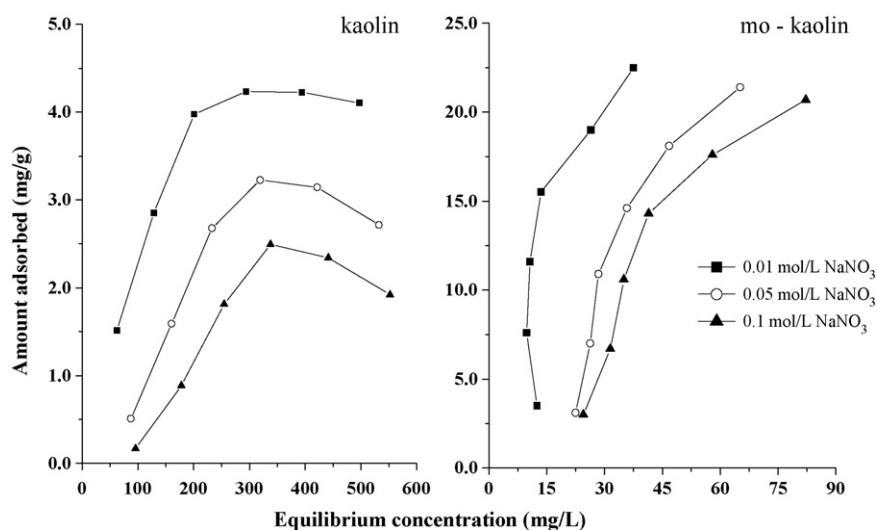


Fig. 2. Effect of initial ion concentration on the adsorption of Pb(II) by the adsorbents. Contact time: 1 h; agitation speed: 150 rpm; dose of each adsorbent: 25 g/L; ionic strength: 0.01 mol/L; temperature of solution: 30 °C.

Table 1

The parameters for Langmuir and Freundlich isotherms.

Parameters	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	n (g/L)	R^2
Raw kaolin	4.73	3.00×10^{-2}	0.997	0.808	3.42	0.867
Modified kaolin	32.2	5.04×10^{-2}	0.998	6.94	3.56	0.882

R^2 = correlation coefficient.

tration of the competing salt is decreased. This might indicate that the adsorption interaction between the functional groups of the adsorbent and the metal cations were mainly ionic in nature, which is consistent with an ion-exchange mechanism. The second factor is the influence of the ionic strength on the activity coefficients of lead ions, which limit their transfer to the adsorbent surfaces. Pb(II) adsorption by kaolin was considered to be primarily due to coulombic attraction of the Pb(II) by permanent negative charges on the minerals [29]. For this reason, Pb(II) adsorption by the adsorbent was strongly influenced by the ionic strength of solution.

3.1.4. Effect of initial metal ion concentration

Initial Pb(II) concentration was adjusted in the ranges of 50–800 mg/L for adsorption on the modified and 50–750 mg/L for the unmodified kaolin under natural pH at 30 °C for 1 h as shown in Fig. 3. The increasing initial Pb(II) concentration resulted in an increase in the Pb(II) adsorbed for both modified and unmodified kaolin. The removal percentage of Pb(II) by the modified sorbent increased rapidly with increase in the Pb concentration in the range of 50–800 mg/L, while increased slowly for the unmodified sorbent and nearly approached to equilibrium when the Pb(II) concentration reached 250 mg/L. At the concentration of 50 mg/L, Pb(II) in the solution would interact with the binding sites and thus facilitated more than 70% adsorption for both the modified kaolin and the natural kaolin, both the Pb(II) adsorbed were 1.4 mg/g. With increasing metal ion concentration, there is an increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on both the modified and unmodified adsorbents [10]. When Pb(II) concentration was 200 mg/L, amount of Pb(II) adsorbed by modified kaolin was 7.5 mg/g compared with 3.6 mg/g by the unmodified sorbent. At higher concentrations, more Pb(II) was left un-adsorbed in solution due to the saturation of binding sites. However, there is a decrease in the active

sites on the sorbents as more metal ions are adsorbed, when the saturated adsorption mass was more than 32 mg/g for modified kaolin, that was only 4.7 mg/g for the unmodified sorbent. This indicates that there are much more active sites on the modified kaolin than the unmodified sorbent, sorption of lead ions is more favourable on the modified sorbent than that on the unmodified adsorbent.

3.2. Adsorption isotherms

The relative values of Q_0 , b , K_f and n obtained as calculated from Langmuir and Freundlich models of Pb(II) on both unmodified and modified kaolin are listed in Table 1. The results showed that experimental data are well fitted to the linear Langmuir isotherm. As shown in Table 1, when Langmuir mode was used to described the adsorption of Pb(II) onto modified and unmodified kaolin, the

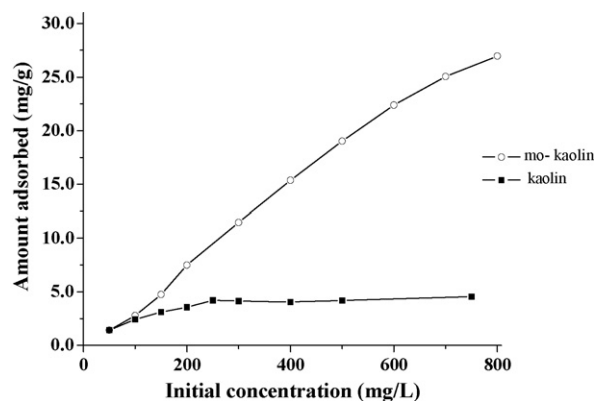


Fig. 3. Effect of ionic strength on the adsorption of Pb(II) on the adsorbents. Initial concentration: 500 mg/L; contact time 1 h; agitation speed: 150 rpm; dose of each adsorbent: 25 g/L; temperature of solution: 30 °C.

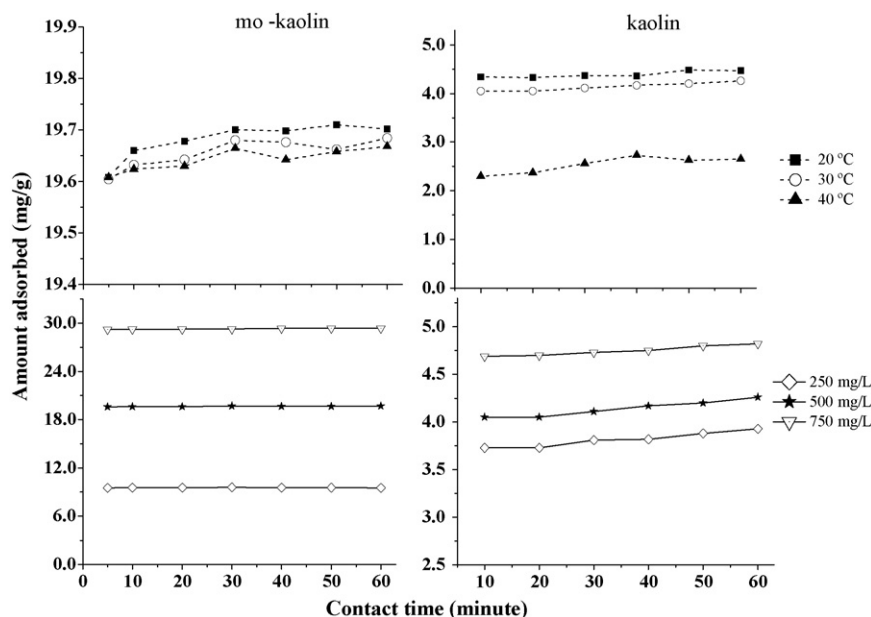


Fig. 4. Effect of initial lead concentration and the temperature on kinetics of Pb(II) adsorption by modified kaolin. Agitation speed: 150 rpm; dose of each adsorbent: 25 g/L; ionic strength: 0.01 mol/L.

linear plot of C_e/Q_e vs. C_e with regression coefficients $R^2=0.998$ and 0.997 were obtained, and the maximum adsorption capacity of modified and unmodified kaolin for Pb(II) was calculated to be 32.2 and 4.73 mg/g, respectively. Simultaneously, the linear plot of $\log Q_e$ vs. $\log C_e$ with regression coefficients $R^2=0.882$ and 0.867 were obtained, and the Freundlich constant K_f of modified and unmodified kaolin for Pb(II) were calculated to be 6.94 and 0.808, respectively. In each case, the value of n was greater than one, indicating that adsorption was favourable. Similar results also were observed in earlier studies of the adsorption of heavy metal ions fitted well to Langmuir isotherm [30]. On the basis of these results, it is concluded that the adsorption coefficients agree well to support favourable adsorption. The Langmuir monolayer capacity is large in conformity with its capacity to take up more of the metal ions [9]. Both the Langmuir and Freundlich constants suggested that the modified kaolin had a much better adsorption

capacity than that of the unmodified kaolin for Pb(II) in aqueous solution.

3.3. Kinetics of Pb(II) adsorption

The kinetics of Pb(II) adsorption by modified and unmodified kaolin was examined. The effect of initial Pb(II) concentration and the temperature on the Pb(II) adsorption are presented in Fig. 4, where the adsorption capacity of modified and unmodified kaolin clay is a function of time and initial Pb(II) concentration and the temperature. For both adsorbents, the amount of Pb(II) uptake, Q_e (mg/g) increased with increase in contact time in tested range of initial Pb(II) concentrations as described in previous section. However, with the temperature increasing, the Pb(II) uptake by modified kaolin slightly changed, while the Q_e by unmodified kaolin decreased.

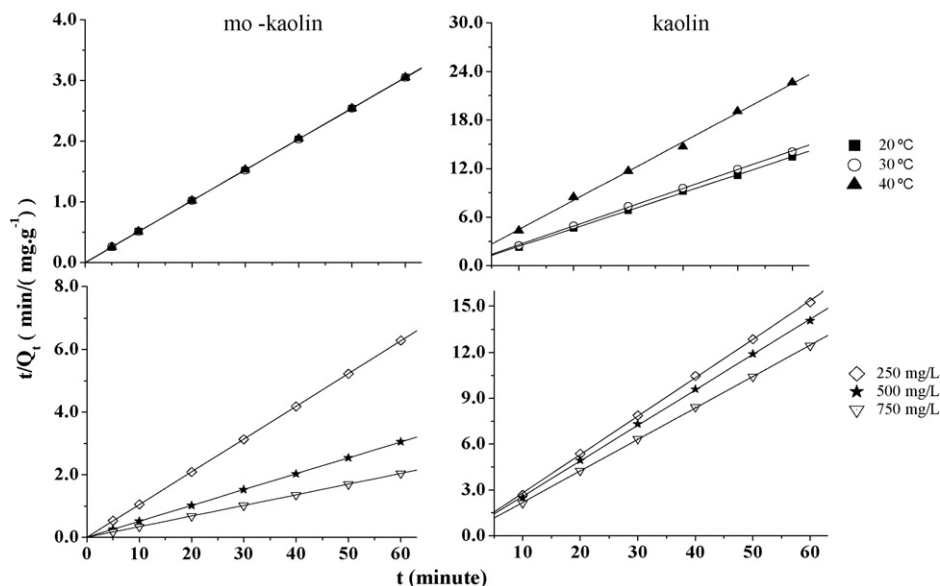


Fig. 5. Pseudo-second-order plots for the adsorption of 500 mg/L of Pb(II) at varying temperature and with varying concentrations at 30 °C.

The adsorption of Pb(II) onto modified and unmodified kaolin was investigated in terms of the kinetics of adsorption mechanism by using pseudo-second-order. Fig. 5 shows a linear variation of t/Q_t with time t (Eq. (4)) at different initial Pb(II) concentrations and different temperatures, respectively. The initial sorption rate h , pseudo-second-order rate constant k , amount of Pb(II) adsorbed at equilibrium Q_e obtained from the pseudo-second-order model and the linear correlation coefficient R^2 are given in Table 2. Increasing Pb(II) concentration increased the initial sorption rate h from 357 to 435 mg/g min⁻¹ for modified kaolin and 3.49 to 4.47 mg/g min⁻¹ for unmodified kaolin as Pb(II) concentration increased from 250 to 750 mg/L. The amount of Pb(II) adsorbed at equilibrium was also found to follow this trend with modified clay showing an increase in Q_e from 9.57 to 29.4 mg/g and unmodified clay from 3.98 to 4.85 mg/g with Pb(II) concentration increased. The increased initial sorption rate h , and the increased amount of Pb(II) adsorbed is expected as increased initial Pb(II) concentration produces a higher driving force that should result in a more rapid change in the rate at which Pb(II) is adsorbed initially onto both the modified and the unmodified kaolinite clay adsorbents. However, there was an observed decrease in the pseudo-second-order rate constant, k , from 3.90 to 0.503 g/mg min⁻¹ for modified kaolin and from 0.220 to 0.190 g/mg min⁻¹ for natural kaolin. This trend indicates that the time for the adsorption of Pb(II) to reach equilibrium is extended with increased initial Pb(II) concentration.

Increase in temperature in the range of 20–40 °C resulted in the decrease in the rate constant, k , from 1.71 to 0.890 g/mg min⁻¹ for modified clay and 0.287 to 0.150 g/mg min⁻¹ for unmodified clay. In addition, the initial sorption rate also decreased from 667 to 345 mg/g min⁻¹ for the modified kaolin and 5.87 to 1.15 mg/g min⁻¹ for unmodified kaolin. While the amount of Pb(II) adsorbed at equilibrium was only a slight decrease, which was found to be still 19.7 mg/g for modified kaolin but decreased from 4.51 to 2.78 mg/g for unmodified adsorbents, respectively, when the temperature increased from 20 to 40 °C. This indicates that temperature has little effect on the Pb(II) adsorbed by modified kaolin but obviously has effect on the unmodified one. The linearity of the plots of the pseudo-second-order model is presented in Fig. 5, which indicates that chemical reaction rather than physi-sorption is the main rate-controlling step throughout most of the adsorption process [15].

3.4. Thermodynamics of Pb(II) adsorption

The plots of $\ln K_d$ against $1/T$ are shown in Fig. 6. The values of ΔH° and ΔS° of Pb(II) adsorption were calculated by fitting the experimental data to Eq. (6) as shown in Fig. 6. ΔG° values were obtained by using Eq. (7). The thermodynamic parameters for the adsorption of Pb(II) were given in Table 3. The negative value of enthalpy change, ΔH° , 4.56 and 22.6 kJ/mol for modified and unmodified adsorbents, indicated that the adsorption of Pb(II) on both adsorbents were exothermic process with adsorption onto unmodified adsorbent being more exothermic. The value of ΔS° , for modified and unmodified kaolin was -8.21 J/mol K⁻¹

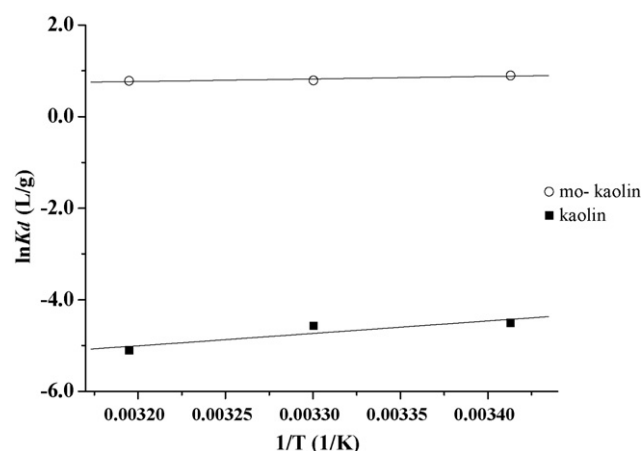


Fig. 6. Relationship between $1/T$ and $\ln K_d$ for modified and raw kaolin (Pb(II) = 500 mg/L).

Table 3

Thermodynamic parameters for the adsorption of 500 mg/L Pb(II) onto modified and unmodified kaolin.

	ΔH° (kJ/mol)	ΔS° (J/mol K ⁻¹)	ΔG° (kJ/mol)		
			20 °C	30 °C	40 °C
Mo-kaolin	-4.56	-8.21	-2.15	-2.07	-1.99
Natural kaolin	-22.6	-114	10.8	11.9	13.1

and -114 J/mol K⁻¹, respectively. It indicated that Pb(II) in bulk phase (aqueous solution) was in a much more chaotic distribution compared to the relatively ordered state of solid phase (surface of adsorbent). The Gibbs free energy ΔG° , listed in Table 3, as calculated for adsorption of Pb(II) on modified and unmodified kaolin was -2.15 , -2.07 , -1.99 kJ/mol and 10.8 , 11.9 , 13.1 kJ/mol, respectively, when the temperature was set at 293, 303, and 313 K. This suggested that the adsorption of Pb(II) onto modified adsorbent was feasible and spontaneous thermodynamically, however, the positive change of ΔG° indicated that the adsorptive forces were not strong enough to break the potential and shift the reaction ultimately to the right leading to binding of Pb(II) onto the surface constituents of the unmodified adsorbent [15]. In addition, amount of Pb(II) adsorbed at three different temperatures showed an decreasing trend with increase in temperature accompanied by decrease in entropy and increase in Gibbs energy suggested that the adsorption of Pb(II) onto modified and unmodified kaolinite clay was less favorable at higher temperatures.

3.5. Removing the metal ions from wastewater

The modified and unmodified kaolins were used to dispose the actual wastewater to test the possibility of metal ions removal, where the wastewater collected was from a plating factory of Fuzhou. 0.5 g of the modified and unmodified kaolins was added to

Table 2

Pseudo-second-order rate constant for the adsorption of varying concentration of Pb(II) at varying temperature on modified kaolin.

Concentration (mg/L)	R^2		Q_e (mg/g)		k (g/mg min ⁻¹)		h (mg/g min ⁻¹)	
	Mo-kaolin	Kaolin	Mo-kaolin	Kaolin	Mo-kaolin	Kaolin	Mo-kaolin	Kaolin
250	1.00	0.999	9.57	3.98	3.90	0.220	357	3.49
500	1.00	0.999	19.7	4.31	1.08	0.209	417	3.87
750	1.00	0.999	29.4	4.85	0.503	0.190	435	4.47
Temperature (°C)								
20	1.00	0.999	19.7	4.51	1.71	0.287	667	5.87
30	1.00	0.999	19.7	4.31	1.08	0.209	417	3.87
40	1.00	0.998	19.7	2.78	0.890	0.150	345	1.15

Table 4
Removal of metal ions from real wastewater by modified and unmodified kaolin.

(Units: mg/L)	Pb(II)	Zn(II)	Ni(II)	Cu(II)	Cr (total)
Initial concentration	178	250	8.30	25.8	67.1
Treated by raw kaolin	168	242	7.10	24.7	63.4
Treated by mo-kaolin	27.5	236	6.30	24.2	56.3

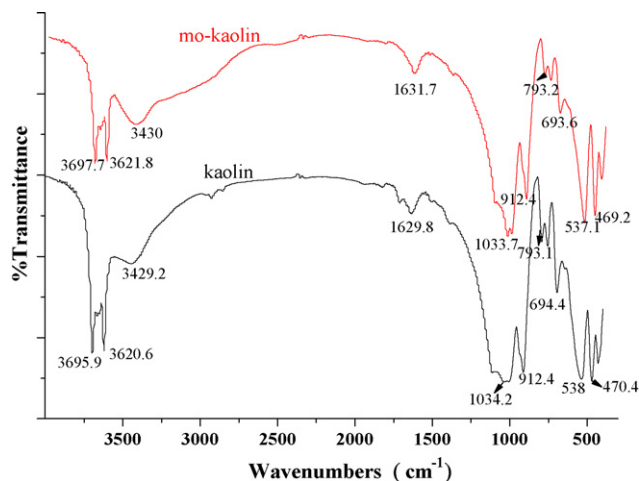


Fig. 7. FTIR spectra for the kaolin and modified kaolin.

20 mL of wastewater in 50 mL polyethylene bottles, respectively, the admixture was shaken at 150 rpm for 1 h. The results determined by AAS are listed in Table 4. From the data the adsorption capability of kaolin for metal ions in actual wastewater was improved using modified kaolin, especially for Pb(II). The concentrations of Pb (II), Cu(II), Ni(II), Cr(total) and Zn(II) was reduced from 178 to 27.5 mg/L, 25.8 to 24.2 mg/L, 8.3 to 6.3 mg/L, 67.1 to 56.3 mg/L and 250 to 236 mg/L, respectively when modified kaolin was added in this wastewater, as compared to 168, 24.7, 7.10, 63.4 and 242 mg/L, respectively when raw kaolin was added. This indicates clearly that the kaolin clay modified with aluminium sulphate has a high selective adsorption to Pb(II) compared with the unmodified kaolin, however, other metal ions such as Ni(II) and Zn(II) were difficult to remove using either modified or unmodified kaolin.

3.6. Characterization of kaolin

The infrared spectrum (400–4000 cm^{-1}) of both unmodified and modified samples was obtained which are presented in Fig. 7. The absorption band at 3695.9 cm^{-1} for the unmodified sample repre-

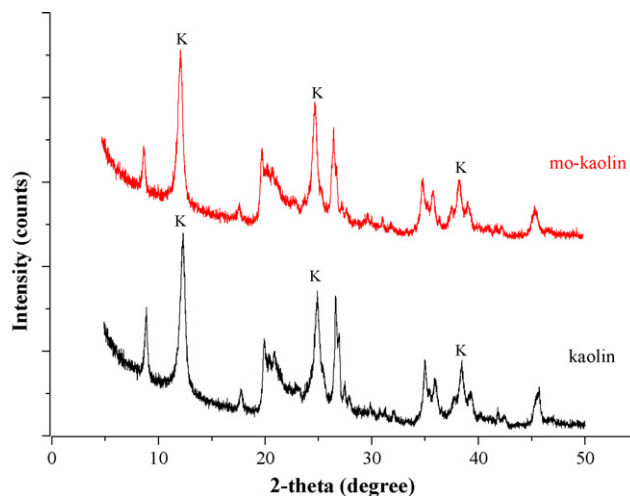


Fig. 8. XRD pattern for the kaolin and modified kaolin.

sents the inner surface–OH stretching vibration and those at 1034.2, 912.4 and 793.1 cm^{-1} represent the Si–O, Al–OH bending vibrations and Si–O stretching of cristobalite, respectively [10,31]. The absorption band at 1629.8 and 470.4 cm^{-1} represent OH bending of water and Si–O–Si deformation/Fe–O stretching, while the bands at 538 and 3620.6 cm^{-1} are due to Al–O–Si stretching vibration and stretching vibration of structural OH groups of kaolinite. Water in kaolinite give a broad band at 3429.2 cm^{-1} corresponding to the H₂O-stretching vibrations [32]. An increase in wavenumber from 1629.8 and 3695.9 cm^{-1} in the unmodified sample to 1631.7 and 3697.7 cm^{-1} , respectively, in the modified sample was observed. The latter peaks were broader and more intense. This suggests that the modification may have been effected on the OH bending of water and the inner surface–OH stretching vibration. The small shift in the 694.4 cm^{-1} peak in the unmodified sample to 693.6 cm^{-1} in modified sample also confirms the involvement of the Si–O bond linkage in the modification [10].

The XRD patterns of modified and unmodified kaolins are given in Fig. 8. The prominent peak found in the kaolinite clay appears at 13.53° and 25° (2θ), the common trend can be seen in contrast of Fig. 8. Meanwhile, Al related species cannot be seen in Fig. 8 (mo-kaolin), which indicates that aluminium sulphate did not impregnate the clay surface.

The morphology of modified and unmodified kaolin examined by scanning electron microscope (SEM) which was used to check the solid morphology and average crystal size of the clay. As shown in Fig. 9, the shape of unmodified kaolin seems to be formed by

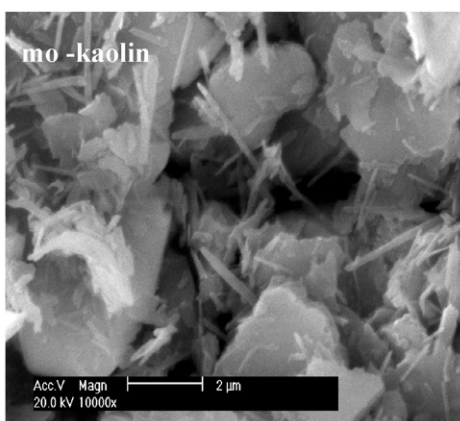
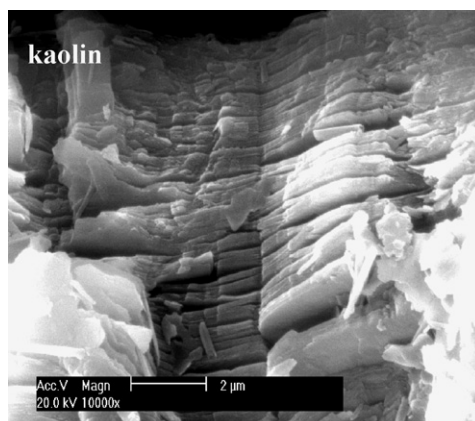


Fig. 9. ESEM images of the kaolin and modified kaolin.

dense sheets. However, the flaky structure of unmodified kaolin was changed into fractional and acerosse structure resulted in the modification. After the modification and calcinations, the layers of unmodified kaolin were broken, leading to more micro-sized particles and bigger specific surface. In addition, aluminium sulphate added to the kaolin could be improves the ion exchange capacity as the composition of modified kaolin did change. Furthermore, the addition of active carbon also improves the sorption capacity since the active carbon can be used as an adsorbents [4–7].

4. Conclusion

In this work, the results obtained from unmodified kaolin used for Pb(II) removal from aqueous solution demonstrated that modified kaolin can enhance the Pb(II) removal, and it could be a potential adsorbent to remove Pb(II) from real wastewater. The amount of Pb(II) adsorbed by modified kaolin was more than four times higher than that of the unmodified kaolin. In addition, the adsorption of Pb(II) by both modified and unmodified kaolin followed the Langmuir model. The linearity of the plots of the pseudo-second-order model indicated that Pb(II) adsorbed by modified kaolin was a main chemical reaction rather than physisorption. Furthermore, The negative value of enthalpy change, ΔH° , and Gibbs free energy change, ΔG° , indicated that the adsorption of Pb(II) onto modified kaolin was a thermodynamically feasible, spontaneous and exothermic process.

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