

Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite

Hao Chen^{a,b}, Yaogang Zhao^a, Aiqin Wang^{a,*}

^a Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, PR China

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Abstract

A series of activated palygorskite clay by HCl with different concentrations was prepared and applied as adsorbents for removal of Cu(II) from aqueous solutions. The effects of contact time, adsorbent dosages and pHs of suspension on the adsorption capacities for Cu(II) were investigated. The results showed that adsorption capacity of activated palygorskites increased with increasing the HCl concentration and the maximum adsorption capacity with 32.24 mg/g for Cu(II) is obtained at 12 mol/L of HCl concentration. The variations in IR spectra and pH of solution after adsorption Cu(II) confirmed that the numerous amount of silanol groups (Si–OH) originated by acid treatment were mainly responsible for Cu(II) adsorption onto acid-activated palygorskite. Kinetic studies indicated that the adsorption mechanisms in the Cu(II)/acid-activated palygorskite system followed the pseudo-second-order kinetic model with a relatively small contribution of film diffusion. Equilibrium data fitted well with Freundlich isotherm model compared to Langmuir isotherm model, indicating that adsorption takes place on heterogeneous surfaces of the acid-activated palygorskite. Adsorption–desorption studies presented that activated palygorskite has lower adsorption and desorption efficiencies using Cu(CH₃COO)₂ than that of other inorganic copper salts, such as CuSO₄, Cu(NO₃)₂, and CuCl₂.

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1. Introduction

Adsorption of metal ions onto clay minerals has been studied extensively because both metal ions and clays are common components in nature and also because a knowledge of the adsorption process could aid in the environmental remediation of water that is polluted by heavy metal ions. Clay minerals usually possess negative surface charge and high surface area [1], which is benefit for the adsorption of heavy metals from solution. Among heavy metals, such as Pb, Cd, Cu, Ni, and Cr, etc., the removal of Cu from aqueous solution has been investigated using many kinds of clay minerals, such as montmorillonite [2,3], kaolinite [4,5], sepiolite [6], and illite [7], etc. In earlier studies, adsorption mechanisms for Cu(II) on clay mineral surfaces are commonly modeled as cation exchange, i.e. outer-sphere complexation [8].

Recent research has shown that inner-sphere complexation of Cu(II) with clay mineral surfaces can also occur and this kind of adsorption model has been observed in studies for the adsorption of Cu(II) onto many minerals [2,5,6,9]. For example, an important adsorption mechanism, which the adsorption of Cu(II) on surface Si–OH sites on the broken edges of sepiolite with simultaneous release of protons, has been suggested for the adsorption of Cu(II) from aqueous solutions to the mineral particles [6]. Hizal et al. [5] also believed that silanol and aluminol surface sites of kaolinite-based clay were responsible for the Cu(II) adsorption through forming monodentate and bidentate surface complexes. Furthermore, desorption studies showed that inner-sphere complexes are more stable than outer-sphere complexes [10].

Palygorskite is a crystalline hydrated magnesium silicate with a fibrous morphology. It is known to contain a continuous two dimensional tetrahedral sheet, but differs from other layer silicates in lacking continuous octahedral sheets. The tetrahedral basal oxygen atoms invert apical direction at regular intervals

* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.
E-mail address: aqwang@lzb.ac.cn (A. Wang).

coordinating talc like ribbons. Each talc-like ribbon alternates with channels along the fiber axis [11]. Its porous structure and absorbed cations provide it with large specific surface area and moderate cation exchange capacity, which is very beneficial for the adsorption of heavy metals from solution. Up to now, few works related to Cu(II) adsorption on palygorskite have been reported [12–14]. Those studies mainly focused on the effect of removal for Cu(II), however, the interactions of mineral–metal interface were less. In order to improve utilization of this mineral as adsorbent, a deeper understanding for this adsorption process is very important.

Acid activation is the usual method employed for improving the surface properties of clay minerals [15,16]. For palygorskite clay, acid activation can modify the number of adsorption sites by disaggregation of palygorskite particles, eliminate mineral impurities and increase its surface area [17]. This process leads to almost full removal of carbonate minerals and partially diminishes the magnesium, iron and aluminium content of palygorskite clay. Moreover, considerable amounts of silanol groups (Si–OH) onto palygorskite surface compared to other layer silicates can be obtained during acid treatment [17,18], which could substantially influence adsorption capacity and mechanism of heavy metal on minerals. Based on the above considerations, it is necessary to improve the knowledge of the effect of acid activation methods on the Cu(II) adsorption capacity of acid-activated palygorskite in mineral–solution system. To our knowledge, so far there has been no report in the literature of the study of the interaction between Cu(II) and the acid-activated palygorskite.

The aim of this paper is to examine the effectiveness and of the acid-activated palygorskites in removing Cu(II) from aqueous solution and determine adsorption characteristics of Cu(II) onto the acid-activated palygorskite. The effects of factors, such as contact time, adsorbent dosage and pH of suspension were investigated. The kinetics and mechanism of Cu(II) adsorption on the adsorbent were also studied. The desorption efficiency and reuse capacity of the adsorbent were also assessed for five successive adsorption–desorption cycles.

2. Experimental

2.1. Materials and chemicals

The palygorskite clay (supplied by Linze Colloidal Co., Gansu, China) was milled into a size of 200-mesh. Chemical composition of the sample in weight percentage of oxides was determined by the PANalytical Company with a Magix PW 2403 XRF Spectrometer and as follows: SiO₂ (57.06); Al₂O₃ (16.59); Fe₂O₃ (6.11); MgO (8.63); CaO (4.55); Na₂O (1.35); K₂O (3.51); TiO₂ (0.71); MnO (0.08); SO₃ (0.42) and P₂O₅ (0.22). A stock solution of Cu(II), prepared by dissolving Cu(CH₃COO)₂·H₂O in double distilled water, was taken as the adsorptive solution. Other agents used, such as HCl, NaOH, CuCl₂·2H₂O, Cu(NO₃)₂·H₂O, CuSO₄·5H₂O, were all of analytical grade and all solutions were prepared with double distilled water.

2.2. Preparation of acid-activated palygorskites

A series of acid-activation palygorskite were performed as follows: 10.0 g palygorskite micro-powder was immersed in 100 ml HCl solution with various concentrations (2, 4, 6, 8, and 12 mol/L) at 20 °C for 2 h under mechanical stirring at 1250 rpm, and then washed with distilled water for many times until pH of 6.0 was achieved. The resulting sample was dried at 105 °C to constant weight and ground into a size of 200-mesh.

2.3. Adsorption procedure

Adsorption experiments were carried out by mixing known amounts of adsorbent with 20 ml of aqueous solution of copper acetate of the desired concentration and shaking in a thermostatic shaker bath (THZ-98A) with 120 rpm at 30 °C for a given time (Shaking time was 4 h except for the study about effect of contact time). The pH of suspension was adjusted with dilute HCl or NaOH solution (Mettler Toledo 320 pH meter). 0.15 g was selected as added amount of adsorbent except for the study about effect of adsorbent dosage. The pH of suspension was adjusted to 6.0 except when the effect of pH was studied. After a shaking time completed, the suspension was centrifuged at 5000 rpm for 20 min. The initial concentration of Cu(II) solutions were all of 500 mg/L in the above experiments.

Adsorption mechanisms were studied according to the pre-defined procedure with Cu(II) concentrations ranging from 25 to 1500 mg/L. The initial and the final concentration of Cu(II) in the acetate solution were measured with an atomic absorption spectrophotometer (Perkin-Elmer SIMAA 6000). The adsorption capacity of Cu(II) was calculated through the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the adsorption capacity of copper on adsorbent (mg g⁻¹), C_0 the initial concentration of Cu(II) solution (mg/L), C_e the equilibrium Cu(II) concentration in solution (mg/L), m the mass of adsorbent used (g) and V is the volume of Cu(II) solution (L). All assays were carried out in triplicate and only mean values were presented.

2.4. Desorption and regeneration studies

The adsorbent utilized for the adsorption of an initial metal concentration of 1500 mg/L was separated from the Cu(II) solution by centrifugation. The Cu(II)-loaded adsorbent was washed thoroughly with 20 mL double distilled water to remove any unadsorbed Cu(II) and then carried out by shaking with 20 mL of 0.1 mol/L HCl solution at 30 °C for 4 h. After this, the adsorbent was washed three times with double distilled water, and then dried and reused for adsorption studies. The adsorption–desorption process was performed in five times. Besides Cu(CH₃COO)₂, CuCl₂, Cu(NO₃)₂, and CuSO₄ were also selected to carry out the adsorption–desorption experiments. The Cu(II) contents of the desorbed solutions was determined as mentioned above.

2.5. Experiments and methods of characterization

The cation exchange capacities (CEC) of the samples were determined by the ammonium acetate method [19]. The specific surface areas (SSA) of the samples were measured by the glycol dimethyl ether (C₄H₁₀O₂) method [20]. The point of zero charge (pH_{PZC}) of the acid-activated palygorskite sample was determined by the solid addition method [21].

FT-IR spectra measurements were done on a Thermo Nicolet NEXUS TM spectrophotometer using the KBr pellets. The spectrum was collected 32 times and corrected for the background noise.

3. Results and discussion

3.1. Effect of HCl concentration

The influence of HCl concentration on the adsorption of Cu(II) onto acid-activated palygorskite was investigated and the results were shown in Table 1. The results showed that q_e increases gradually with the increase in HCl concentration and a maximum of the q_e was observed at HCl concentration of 12 mol/L. As seen in Table 1, CEC and SSAs of the acid-activated samples decrease and increase significantly with the increase in HCl concentration compared to that of natural palygorskite clay, respectively. This suggests that the SSA is a main factor for Cu(II) adsorption onto acid-activated palygorskite.

Specific adsorption (inner-sphere complexation) can be described by a surface complexation model which defines surface complexation formation as a reaction between functional surface groups (Si–OH) and an ion in a surrounding solution, which form a stable unit [22]. According to mechanism of acid treatment [17], the relative abundance of Si–OH groups along the direction of the palygorskite fibres increases evidently with acid concentration [18]. Fig. 1 depicts the IR spectra of palygorskite and the acid-activated palygorskites. It is observed that the absorption bands at 1437, 881, and 728 cm⁻¹ of nature palygorskite clay disappeared after acid treatment, indicating the carbonate mineral contained in palygorskite sample were eliminated [23]. Compared to IR spectra of nature palygorskite, those of the acid-activated palygorskites show a new absorption band at 3730 cm⁻¹, which corresponds to the OH-stretching vibrations of surface silanol groups [24,25]. Moreover, the intensity of the absorption band become stronger with the increase of HCl concentrations, indicating the amount of silanol groups on palygorskite surface become more via acid modification. After

Table 1
Adsorption capacities for Cu(II), pH of final solutions, SSAs and CECs of natural and acid-activated palygorskites

	HCl concentration (mol/L)					
	0	2	4	6	8	12
q_e (mg/g)	26.02	29.14	29.70	30.73	31.64	32.24
pH	5.90	5.79	5.75	5.70	5.67	5.63
SSA (m ² /g)	48.7	192.9	221.2	224.3	234.5	267.5
CEC (meq/100g)	30.0	14.4	13.7	13.6	11.7	9.9

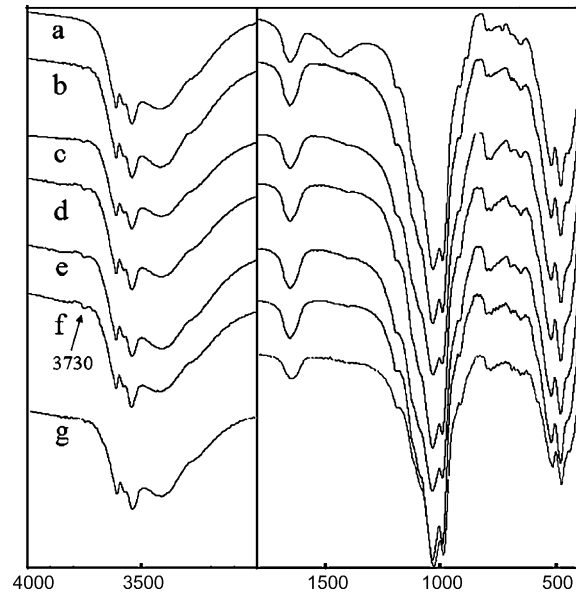
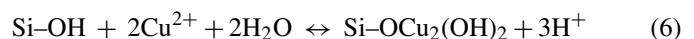
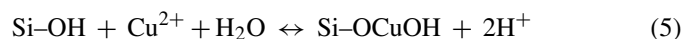
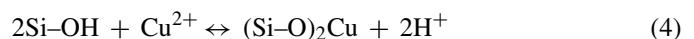
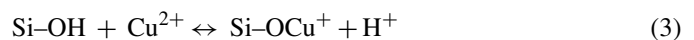
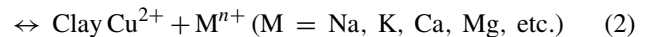
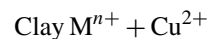


Fig. 1. IR spectra of palygorskite samples activated with HCl of 0 mol/L (a), 2 mol/L (b), 4 mol/L (c), 6 mol/L (d), 8 mol/L (e), 12 mol/L (f), and Cu(II) adsorption onto the palygorskite sample activated 12 mol/L of HCl (g).

Cu(II) adsorption, the absorption band at 3730 cm⁻¹ of the acid-activated palygorskite clearly weakens (Fig. 1(g)), indicating that the silanol groups participated in the adsorption process. It is speculated by the above variation of IR spectra that the inner-sphere complexation model might be the dominating adsorption mechanism for Cu(II) onto acid-activated palygorskite.



The pH of final solution decreases gently with acid-activated palygorskite prepared with the increase of HCl concentration (Table 1). Cation exchange, i.e. the out-sphere mechanism which can be represented by Eq. (2) would induce the increase in pH value of solution due to the lower hydrolyse constant (K_{sp}) of Cu(II) compared to M^{n+} on palygorskite. However, the specific adsorption of surface sites (Si–OH) on the acid-activated palygorskite by Eqs. (3)–(6) can bring a decrease in final pH. It is conceivable that more silanol groups of palygorskite particles produced by increase of HCl concentration can easily form a more stable unit with Cu(II) than cation exchange, and specific adsorption involving monodentate and bidentate complexations onto Si–OH sites of the acid-activated palygorskite particles predominates under the adsorption conditions, which should be an important reason resulting in a gradual increase in adsorption capacity of the acid-activated palygorskite. Based on the above analysis, it is considered that the out-sphere and inner-sphere

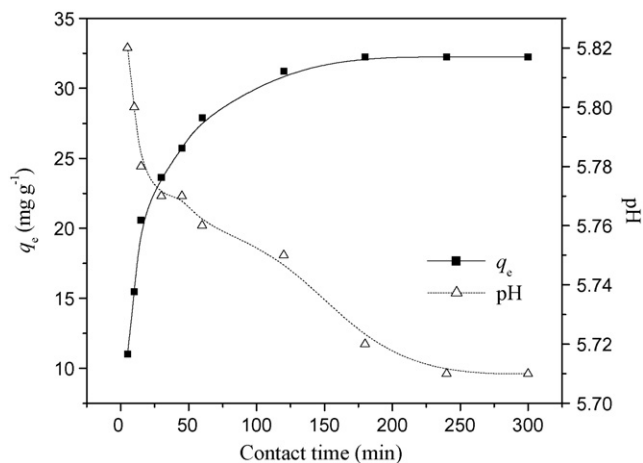


Fig. 2. Effect of contact time on adsorption of acid-activated palygorskite for Cu(II).

adsorption occurred simultaneously during the adsorption process, but the inner-sphere complexation model should be the dominating adsorption mechanism for Cu(II) onto the acid-activated palygorskite. From the above results, palygorskite activated with 12 mol/L HCl was selected as an adsorbent for the rest of the batch experiments.

3.2. Kinetics studies

The effect of contact time on the removal of Cu(II) by acid-activated palygorskite is shown in Fig. 2. As can be seen from the graph, the adsorption of Cu(II) is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate. It shows that maximum adsorption took place at 240 min and there is almost no adsorption beyond the above time. So, 240 min was fixed as equilibrium time throughout this study. The pH of final solution decreases slightly with an increase in contact time, followed by a constant value upon further increasing contact time. The reason caused to this trend in pH may be attributed to specific adsorption mechanism mentioned above. These results indicate that there is a relative long equilibrium time in the present study in comparison to the results reported by other investigators [14,26], who found that the equilibrium time for Cu(II) onto minerals, such as nature palygorskite clay and Ca-rectorite was short (30 and 60 min, respectively). The difference might imply the adsorption sites on the acid-activated palygorskite are not well exposed and there are more complex adsorption mechanisms.

To examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, pseudo first-order and pseudo-second-order kinetic equations were used to test the experimental data. The pseudo-first-order kinetic model was suggested by Lagergren [27] for the adsorption of solid/liquid systems and its linear form can be formulated as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

where q_t is the adsorption capacity at time t (mg g⁻¹) and k_1 (min⁻¹) is the rate constant of the pseudo-first adsorption, was

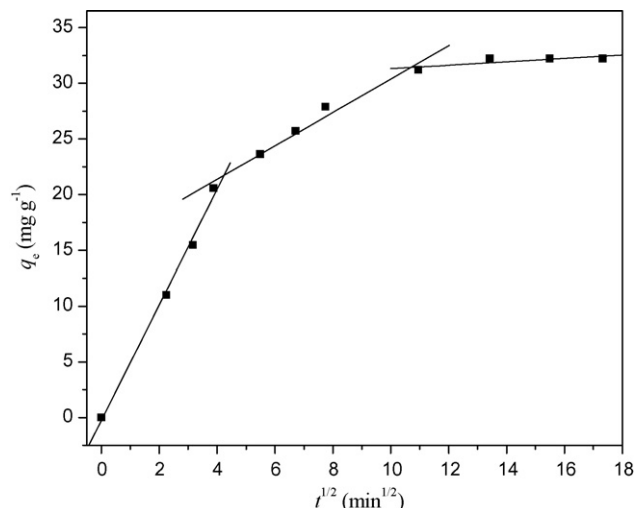


Fig. 3. Intra-particle diffusion kinetic plot for the adsorption of Cu(II) onto acid-activated palygorskite.

applied to the present study of Cu(II) adsorption. The k_1 and correlation coefficient were calculated from the linear plot of $\log(q_e - q_t)$ versus t (figure not shown) and listed in Table 2. It was found that the correlation coefficient for the pseudo first-order kinetic model is very high. However, a large difference of q_e between the experiment and calculation was observed, indicating a poor pseudo-first-order fit to the experimental data.

The kinetic data were further analyzed using Ho's pseudo-second-order kinetics model. It can be expressed as [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order adsorption. Fig. 4 shows the plot of t/q_t versus t for Cu(II) onto acid-activated palygorskite. The k_2 , the calculated q_e value and the corresponding linear regression correlation coefficient r^2 are given in Table 2. A extremely high correlation coefficient (0.999) was obtained. Moreover, the calculated q_e value also agrees with the experimental data in the case of pseudo-second-order kinetics. These suggested that the adsorption data are well represented by pseudo-second-order kinetics. The pseudo-second-order adsorption was also reported for Cu(II) adsorption onto a natural kaolinite clay [29].

The kinetic data can also be analyzed by intra-particle diffusion kinetics model, formulated as [30],

$$q_t = k_i t^{1/2} + C \quad (9)$$

where k_i (mg g⁻¹ min^{-1/2}) is the intra-particle diffusion rate constant and C (mg g⁻¹) is a constant. The values k_i , C and correlation coefficient calculated from the slope of the plot of q_t versus $t^{1/2}$ are shown in Table 2. It was found that the correlation coefficient for the intraparticle diffusion model is lower than those of the pseudo-first-order and the pseudo-second-order models. This indicates that the adsorption of Cu(II) onto the acid-activated palygorskite do not follow the intra-particle diffusion kinetics. However, the plot of q_t versus $t^{1/2}$ can be divided into a multi-linearity correlation (Fig. 3), which indi-

Table 2
 Constants and correlation coefficients of the three kinetic models and those of the two isotherm models

Adsorbent	Pseudo-first-order model			Pseudo-second-order model			Intra-particle diffusion model				
	q_e (exp) (mg g ⁻¹)	k_1 ($\times 10^2$ min ⁻¹)	r^2	q_e (cal) (mg g ⁻¹)	k_2 ($\times 10^3$ g mg ⁻¹ min ⁻¹)	r^2	q_e (cal) (mg g ⁻¹)	r^2	k_i (mg g ⁻¹ min ^{-1/2})	C (mg g ⁻¹)	r^2
Acid-activated palygorskite	32.24	2.665	0.985	22.55	2.373	0.985	34.29	0.999	1.600	10.36	0.876
Langmuir equation											
q_m (mg g ⁻¹)							Freundlich equation				
93.02	b (L mg ⁻¹)			r^2			K_f (L g ⁻¹)			$1/n$	
	1.61×10^{-3}			0.982			0.208			0.86	
										0.989	

cates that three steps occur during adsorption process. For the first sharper portion, i.e. from 0 to 15 min, it is postulated that Cu(II) was transported to the external surface of the adsorbent through film diffusion and its rate, $k_{i1} = 5.188 \text{ mg g}^{-1} \text{ min}^{-1/2}$ shows this adsorption process is very fast. The second portion is the gradual adsorption stage where the intra-particle diffusion with $k_{i2} = 1.503 \text{ mg g}^{-1} \text{ min}^{-1/2}$ can be rate controlling. The third portion (after 120 min) is the final equilibrium stage where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution [31]. From the above analysis, it can be concluded that both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of Cu(II) on the acid-activated palygorskite.

To determine the actual process involved in the present adsorption, Eq. (10) of the adsorption dynamics can be employed [32].

$$F = 1 - \frac{6}{\pi^2} \sum_1^{\infty} \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (10)$$

where F is the fractional attainment of equilibrium at time t and is obtained by using Eq. (11), n Freundlich constant of the adsorbate and B_t is a calculated mathematical function of F (and vice versa) derived from the Reichenberg's table [32].

$$F = \frac{Q_t}{Q_{\infty}} \quad (11)$$

where Q_t and Q_{∞} are amounts adsorbed after time t and after infinite time, respectively.

Rearranging the above equation gives:

$$B_t = -\ln(1 - F) - 0.4799 \quad (12)$$

$$B_t = 6.28318 - 3.2899F - 6.28318(1 - 1.0470F)^{1/2} \quad (13)$$

Eq. (13) was used for values of F from 0 to 0.85 and Eq. (12) for values from 0.86 to 1. Thus, the value of B_t can be calculated for each value of F using Eq. (12) or (13). The B_t values were plotted against t as shown in Fig. 4. The linearity of this plot can be used to distinguish between film diffusion and intra-particle diffusion mechanism [33]. It can be seen from Fig. 4 that the nature of the graph is not a straight line, indicating the film diffusion mechanism is the rate controlling step in a whole adsorption process. However, the linearity of the plot for acid-activated palygorskite is high (0.98). This implies that the film diffusion mechanism shows a relative weak rate control for Cu(II) adsorption onto the acid-activated palygorskite. This result again confirms the mechanism of adsorption stated in intra-particle diffusion kinetic model studies.

3.3. Effect of adsorbent dosage

Effect of the acid-activated palygorskite dosage on q_e and pH of the final solution are presented in Fig. 5. It is observed that q_e decreases with increasing amount of adsorbent. This shows that the amount of Cu(II) adsorbed per unit weight of the acid-activated palygorskite decreases with the increase in adsor-

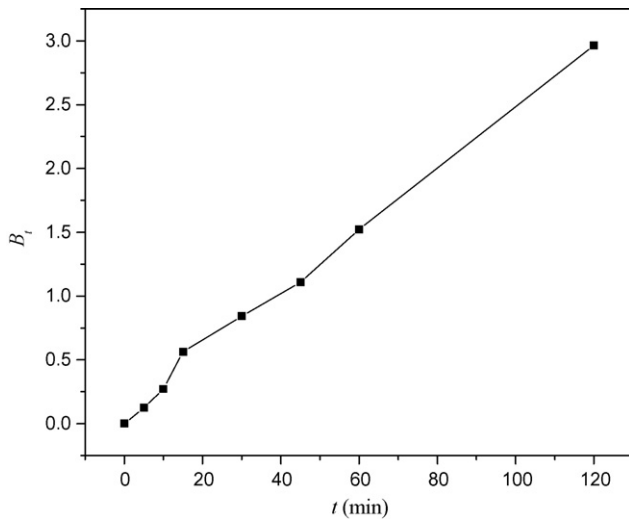


Fig. 4. B_t vs. t plot for Cu(II) adsorption onto acid-activated palygorskite.

bent dosage. The decrease in unit adsorption with increasing adsorbent dosage is basically due to adsorption sites remaining unsaturated during the adsorption reaction [34].

As seen in Fig. 5, pH of the final solution decreases gradually with the increase of the adsorbent dosage. It can be explained by the following fact. The amount of Si–OH adsorption sites on surface of acid-activated palygorskite particles increase with an increasing adsorbent mass, more H⁺ ions were released into solution via inner-sphere complexation and results in an decrease in pH of the final solution.

3.4. Effect of pH of suspension

pH of suspension is an important variable which determines the existent form and the quantity of Cu(II) in water. The form and quantity of mineral’s surface site, sequentially affects the adsorption of the metal at the clay–water interfaces. So, the influence of pH of the initial suspension on Cu(II) adsorption on the acid-activated palygorskite was investigated in the pH range of 2.0–7.0 (Fig. 6). It is clearly seen from the graph that the q_e

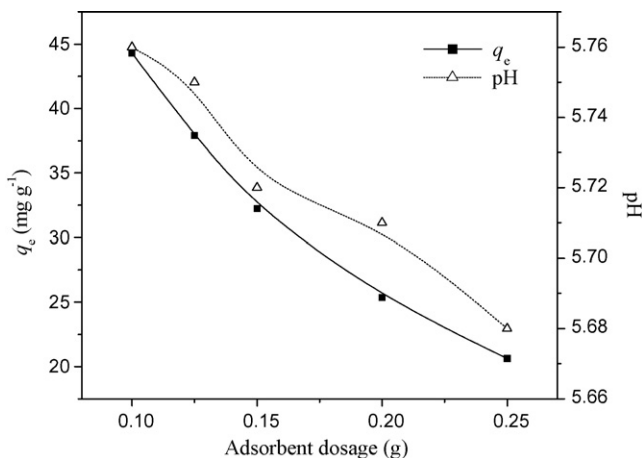


Fig. 5. Effect of adsorbent dosage on adsorption of acid-activated palygorskite for Cu(II).

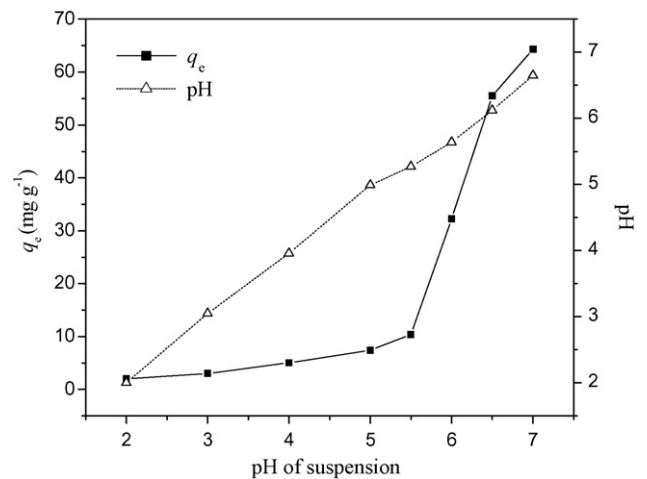


Fig. 6. Effect of pH of suspension on adsorption of acid-activated palygorskite for Cu(II).

increases at a slower rate with an increase in pH of the initial suspension from 2.0 to 5.5, and then increases considerably as the pH increases further. At lower pH, more H⁺ ions compete with Cu(II) and results in the suppression of Cu(II) adsorption on the adsorbent surface, thereby low values of q_e were obtained below the pH of 5.5. As the pH increases further, the positive charge on the adsorbent surface decreases and the number of negatively charged sites increases. In the present experiment the point of zero charge (pH_{pzc}) of the acid-activated palygorskite was measured 4.1, indicating the amounts of positive charge and negative charge on the adsorbent surface at the moment is equal. However, the abrupt increasing point of adsorption capacity does not occur at this pH, this implies that the other mechanism not electrostatic attraction may be operative. As pH increases to 5.5, in fact, it is conceived by the previous studies that large amounts of sites on the adsorbent surface occurred with the form of silanol groups (Si–OH) due to the evident decrease of H⁺ ions in solution, hence, they are available to adsorb more Cu(II) through surface complex reactions, resulting in a sharp increasing adsorption. The Cu(II) adsorption increases slowly again as the pH is closed to neutral. This may be reduce the mobility of Cu(II) due to the decrease in the exchangeable form, resulting in a decrease in the contact probability between adsorbent and adsorbate [35].

From Fig. 6, it can be seen that the final pH increases with the increase in pH of initial suspension. As the pH values of initial suspension exceed to 5.0, the final pH values are all lower than the corresponding pH values of initial suspension. The reason caused to this result has been discussed in the kinetics studies earlier.

3.5. Adsorption isotherm

The adsorption of Cu(II) onto the acid-activated palygorskite is determined in the Cu(II) concentrations ranging from 25 to 1500 mg/L and the corresponding adsorption isotherm is plotted in Fig. 7. The isotherm curve for Cu(II) seems to have increased at high relative concentrations, which makes it difficult to estimate a limiting value at the concentrations studied.

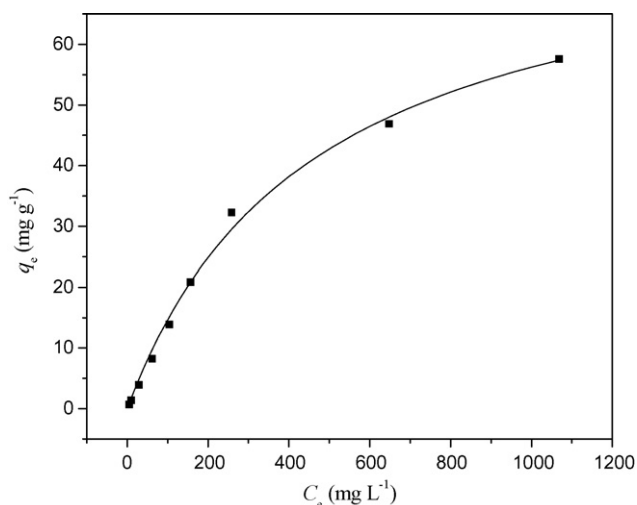


Fig. 7. Adsorption isotherm of Cu(II) onto acid-activated palygorskite.

The adsorption data can then be correlated with the Langmuir [36] and the Freundlich [37] isotherm models equations.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (14)$$

Freundlich equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (15)$$

where q_e is the equilibrium concentration of Cu(II) on adsorbent (mg g^{-1}), C_e the equilibrium concentration of Cu(II) in solution (mg L^{-1}), q_m the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}) and related to the free energy of adsorption. K_f is the Freundlich constant (L g^{-1}) and $1/n$ (dimensionless) is the heterogeneity factor.

The Langmuir and Freundlich parameters for the adsorption of Cu(II) onto the acid-activated palygorskite are listed in Table 2. A better-fitted straight line with high correlation coefficient was obtained in case of Freundlich (Fig. 8), while the linearity of the plot of Langmuir model (figure not shown) is very poor. This suggests that the adsorption data are well represented by Freundlich isotherm model and support the assumption that adsorption takes place on heterogeneous surfaces [37]. Since the parameter $1/n$ is related to the degree of surface heterogeneity (smaller value indicates more heterogeneous surface whereas value closer to or even 1.0 indicates a material with relatively homogenous binding sites) [38], the value of 0.86 obtained for the acid-activated sample suggests that, in spite of the different types of sites (Si–OH, Si–O[−] and remained exchangeable cations, etc.) having different adsorption energy on the surface of palygorskite modified with acid, it is most likely that the numerous amount of silanol groups compared to other sites were responsible for the inapparent heterogeneous adsorption of Cu(II) onto the acid-activated palygorskite. This result further supports the mechanism mentioned in the previous studies.

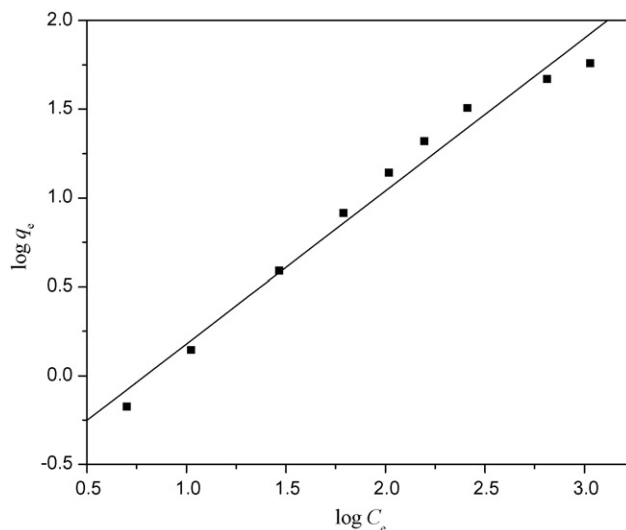


Fig. 8. Freundlich plot for the adsorption of Cu(II) onto acid-activated palygorskite.

The value of maximum adsorption capacity (q_m) calculated from the Langmuir isotherm in this study is very higher than that of those reported in the literature, which different kinds of natural clays were used [14,26,39]. This result indicates that the acid-activated palygorskite possesses a high adsorption capacity so that it is very useful in removing Cu(II) from aqueous solutions.

3.6. Repeated adsorption–desorption studies

Recovery of copper from the loaded adsorbent is necessary for disposal as well as for reuse of the adsorbate. The four types of copper salts were used in the adsorption–desorption experiments. The adsorption and desorption efficiencies of the acid-activated palygorskite are summarised in Table 3. It can be clearly observed from Table 3 that the adsorption efficiency decreases slightly with the increase of cycle times as well as the desorption efficiency for CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 . The desorption is sufficiently high for the three inorganic copper salts.

Table 3
Repeated adsorption–desorption studies for Cu(II) adsorption onto acid-activated palygorskite using different copper salts

Copper salts	No. of cycles					
	1	2	3	4	5	
$\text{Cu}(\text{CH}_3\text{COO})_2$	Adsorbed (%)	48.36	43.55	22.63	21.78	20.64
	Desorbed (%)	62.72	23.24	7.45	5.25	3.64
CuCl_2	Adsorbed (%)	48.47	48.16	48.05	47.64	46.95
	Desorbed (%)	97.70	96.17	92.44	91.91	91.06
$\text{Cu}(\text{NO}_3)_2$	Adsorbed (%)	47.44	46.92	46.78	46.20	45.78
	Desorbed (%)	88.74	88.14	81.19	80.27	79.39
CuSO_4	Adsorbed (%)	47.53	47.22	47.43	47.33	47.12
	Desorbed (%)	90.21	89.79	88.51	86.81	86.38

When $\text{Cu}(\text{CH}_3\text{COO})_2$ was used, both the adsorption and desorption efficiencies decrease sharply with the increase of cycle times. This suggested that species for the same metal may affect the Cu(II) adsorption onto the acid-treated palygorskite and the different adsorption processes maybe occur. Shirvani et al. investigated Cd(II) adsorption on the minerals and found that sorption rate generally decreased in the presence of acetate [40]. From the results of studies, it can be conceived that the difference of adsorption–desorption efficiencies versus cycle time may be related to the property of acetate anions. The reasons for the difference of copper adsorption–desorption on the acid-activated palygorskite using acetate salt and other inorganic salts are not clear and need further study.

4. Conclusions

The present study shows that the acid-activated palygorskite is an effective adsorbent for the removal of Cu(II) from aqueous solution. Acid treatment changed palygorskite clay's physico-chemical properties (CEC and SSA) and mineralogical surface structure. The adsorption capacities of adsorbents for Cu(II) increase with an increase in the HCl concentrations and a maximum was obtained at 12 mol/L of HCl concentration.

Batch adsorption studies, the adsorption capacity of Cu(II) on the acid-activated palygorskite increases with the increase of contact time and pH of initial suspension, but the decrease of adsorbent dosage. The results obtained from IR and pH of final solution suggested that the surface complexation is a dominant adsorption mechanism for Cu(II) onto the acid-activated palygorskite. Adsorption kinetics followed pseudo-second-order kinetic model with a relatively small contribution of film diffusion. The equilibrium experimental data fit well with the Freundlich isotherm. It implies Cu(II) adsorption takes place on heterogeneous surfaces of the acid-activated palygorskite. In the adsorption–desorption experiments, the adsorption and desorption efficiencies were difference using $\text{Cu}(\text{CH}_3\text{COO})_2$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, and CuSO_4 . This suggested that anionic kinds for the same metal may affect the Cu(II) adsorption onto the acid-treated palygorskite.

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