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REMOVAL OF AQUEOUS Cu(II) WITH NATURAL KAOLIN: KINETICS AND EQUILIBRIUM STUDIES

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Abstract

Copper pollution is common across the world and has caused serious public health problems recently. Among the conventional methods, adsorption has proved effective, economic, versatile and simple for the removal of aqueous Cu(II) contaminants. Deposits of natural Kaolin are abundant around the world, and are regarded as valueless due to its limited usage in industry. In this study, the adsorption behavior of natural Kaolin towards Cu(II) was evaluated. According to the results, the isothermal adsorption data are well fitted with Sips model, and the adsorption capacity of natural Kaolin to Cu(II) is determined to be 76 mg/g. Several factors can affect the adsorption performance of Cu(II), including dosage of adsorbent, initial Cu(II) concentration, solution pH, temperature and contact time. The kinetics data are also well predicted by the pseudo-first order kinetics and the pseudo-second order kinetics; the equation of the intraparticle diffusion model could be considered as a supplement. The thermodynamic behavior reveals the endothermic and spontaneous nature of the adsorption. The mechanism for the adsorption behavior was studied based on XRD spectra, and ion-exchange reaction and surface complexation were regarded as predominant.

Key words: adsorption, complexation, Cu(II), ion-exchange reaction, natural Kaolin

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1. Introduction

Kaolin, as one of the most essential clay minerals in the natural environment, has been utilized as an important additive in many industries, including ceramic, paper manufacturing, rubber processing, plastic and oil painting manufacture. Nevertheless, Kaolin of high purity is always required, while natural Kaolin with impurities is of comparatively less value. Although Kaolin is widely distributed in more than 60 countries, including Great Britain, the USA, Brazil, Australia and China, most of these minerals are natural Kaolin with a certain percentage of impurities, while Kaolin with high purity is rare and precious (Hora, 1998). For example, the Kaolin deposit owned by ECC International in Cornwall (UK) has already been

exhausted (Tang et al., 2009). In view of the enormous mineral reserves and the increasing market competition, it is necessary to broaden the application scope of natural Kaolin by developing new technologies.

Over the years, along with the rapid development of economies, the environment has faced severe heavy metal pollution mainly originating from arbitrary discharge from mining drainage, industrial sewage and domestic sewage directly, that could result in potential threat to living organisms. Among all the highly toxic heavy metals, copper has been given special attention. Cu(II) is an essential nutrient in trace amounts; just the right intake of Cu(II) is necessary for the healthy growth of living creatures, but at higher levels it is toxic for plants, algae and humans (Ouyang

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et al., 2008). For example, copper plays a primary carcinogenic role among copper-smiths and the presence of a high Zn:Cu ratio in the soil can cause stomach cancer (Ho et al., 2001). According to the drinking water standard proposed by US Environmental Protection Agency, the concentration of Cu(II) should be lower than 1.3 mg/L (USEPA, 2009). The European Union, WHO and Australia recommend that the upper limit of Cu(II) in drinking water should be 2 mg/L (Australia, 2011; EU, 1998; WHO, 2011).

Conventional treatment methods towards Cu(II) containing wastewater include precipitation, ion exchange, adsorption, coagulation, evaporation, redox, membrane separation and extraction (Bulgariu et al., 2009; Fan et al., 2006; Tang et al., 2010, 2012; Uslu and Tanyo, 2006). In practice, the process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economic, versatile and simple (Bansal et al., 2016; Gavrilescu, 2004; Khalil et al., 2016; Kicsi et al., 2010; Lupascu and Ciobanu, 2009). Given the need to circumvent these contamination problems and the reality of abundant distribution of Kaolin across the world, one approach for removing Cu(II) by Kaolin has recently been proposed.

However, it appears that further research on natural Kaolin, which is very common in mineral deposits and also is the original state of Kaolin in the environment, is necessary. Furthermore, studying the environmental character of natural Kaolin will be conducive to our understanding of soil health and living surroundings. In this study, the adsorption behavior of Cu(II) on natural Kaolin are investigated. The governing mechanisms are discussed, as well as several influencing factors including slurry concentration, temperature, contact time, solution pH, mineral component.

2. Experimental section

2.1. Materials

The natural Kaolin sample used in the experiment was purchased from Sinopharm Ltd (China). All the other inorganic compounds were analytical grade. A stock solution was prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (ZHENXIN, China) in deionized water to produce a 1 M standard solution, which was stored in a refrigerator at around 4 °C. Before the test, the 1 M standard solution was diluted by deionized water to the target concentrations for use. Conical flasks and PVC tubes (Polyvinylchloride Centrifuge Tubes) were immersed in 0.01 M HNO_3 solution overnight then rinsed three times with deionized water.

2.2. Characterization of adsorbent

The elemental constituent (Zn, Pb, Fe, Mg, Ca, K, Na, Al) of the Kaolin sample was determined by Atomic Absorption Spectroscopy (AAS, Hitachi 180-

80, Japan) after 1 g of the sample was digested by a HF: HNO_3 (1:1) mixture completely.

The specific surface area of the natural Kaolin was determined by the N_2 adsorption method (Autosorb 1-MP apparatus, Quantachrome Corporation, USA) (Do, 1998; Tan, 1995). The results were analyzed using the BET adsorption theory to predict parameters including the surface area, volume of micropores and average pore size.

The pH of Kaolin samples was measured by glass electrode potentiometer (pH 213, China) following the method used by previous works (Tang et al., 2017). XRD spectra of the adsorbents (natural Kaolin and Cu(II) laden kaolin) were obtained by D/MAX-RA apparatus (Rigaku Corporation, Japan) with the assistance of engineers from the Analytical and Testing Center of Zhejiang University.

2.3. Batch test

2.3.1. Effect of dosage

The dosage of the adsorbent (natural Kaolin) in the aqueous solution was increased from 0.5 to 1, 5, 10, 20 and 40 g/L to investigate the effect of slurry concentration. Cu(II) solutions with varied initial concentrations (60, 120, 240 mg/L) were prepared and transferred into tapped conical flasks. After mixing with the adsorbent, the flasks were put into an agitator with an air conditioner.

Batch adsorption tests were conducted at isothermal conditions (25 °C) for 96 h at 180 rpm (THZ-C-1, BING, China). The solution pH was not adjusted during this test. At the end of the test, the supernatants obtained after centrifugation at 3000 rpm for 5 min (TDZ5-WS, XIANGYI, China) were analyzed by AAS. All samples in this experiment were conducted in duplicate.

2.3.2. Adsorption kinetics

Cu(II) solutions with varied initial concentrations (67, 134, 267 mg/L) were prepared. The slurry concentration of the adsorbent was fixed at 10g/L in this test. Natural Kaolin (0.5 g) was mixed with 50 mL Cu(II) solution in a conical flask which was placed in the agitator to equilibrate at 25 °C. The test was stopped at specific time points increasing from 0 to 2, 8, 16, 24, 48, 96 and 182 hours. The mixture was transferred to polypropylene centrifuge tubes, and then centrifuged at 3000 rpm for 5 min. The Cu(II) concentration of the supernatant was determined afterwards. Duplicate and blank tests were conducted to obtain an average value for each test.

2.3.3. Effect of temperature and thermodynamics

The natural Kaolin (10 g/L) was blended with three sets of copper chloride solution with increasing initial Cu(II) concentrations of 50, 100 and 200 mg/L. The equilibration of the slurry was performed at increased temperatures separately from 5 to 55 °C with increments of 10 °C. In addition, some samples with initial concentrations of 500 and 800 mg/L and 1, 2, 3, 4, 5 g/L were also tested at 55 °C in order to obtain more details on adsorption capacity. The mixtures

were agitated at 180 rpm for 96 hours. The equilibrium Cu(II) concentration was determined using the same method described in the above tests.

2.3.4. Effect of pH

Initially, the adsorbent and Cu(II) solution were separately mixed in nine polypropylene centrifuge tubes, and some parameters were fixed as follows: dosage of adsorbent 10 g/L, initial Cu(II) concentration 100 mg/L. The pH of these nine centrifuge tubes was regulated and ranged from 2.0 ± 0.2 to 10.0 ± 0.2 with increments of 1.0. Every sample was agitated at 180 rpm, 25 °C for 96 hours. The Cu(II) concentration of the supernatants obtained after centrifugation was analyzed by AAS.

3. Results and discussions

3.1. Characterization of the natural Kaolin

Table 1 shows the correlated basic parameters of the natural Kaolin applied in this study. It is obvious that the major elements in natural Kaolin are Al (21.58%), Fe (2.500%), Ca (3.052%), Na (1.352%), Mg (0.476%) and K (0.112%). Cu(II) was not found in the natural Kaolin sample. The results of the N₂ adsorption test showed that the specific surface area of the natural Kaolin was 7.977 m²/g, while the total pore volume and the average pore diameter were 0.05189 mL/g and 260.2 μm, respectively. The pH of natural Kaolin was 6.5, and Cation Exchange Capacity (CEC) was about 7.5 meq/100g.

According to the mass content of iron, the Kaolin could be divided into two varieties: hard Kaolin and soft Kaolin (Hinckley, 1965). The Kaolin used here could be viewed as hard Kaolin because the ferrous content reaches about 2.5%. Fig. 1 shows XRD spectra of natural Kaolin and Cu(II) laden Kaolin. From the characteristic band of natural Kaolin, it can be extrapolated that Kaolinite composes only part of the adsorbent. There also exist other minerals such as mica, white mica, K nepheline and magnesium carbonate, as shown in band (a).

3.2. Effect of dosage

The effect of adsorbent dosage on unit adsorption amount and Cu(II) removal percentage is shown in Fig. 2. The test was conducted at 25 °C without adjusting the solution pH.

Table 1. Basic parameters of natural Kaolin

Element	Unit	Concentration	Weight percent
K	mg/L	2.8	0.112%
Na	mg/L	33.8	1.352%
Ca	mg/L	11.9	0.476%
Mg	mg/L	76.3	3.052%
Al	mg/L	53750	21.58%
Fe	mg/L	62.5	2.500%
Cu	mg/L	NA	NA
Parameter		value	R ²
Specific surface area	m ² /g	7.977	0.9999
Total pore volume	mL/g	0.05189	
Average pore diameter	μm	260.2	
pH _{natural Kaolin}		6.5	-
CEC	meq/100g	7.5	-

The unit adsorption amount decreased as the reduction of initial Cu(II) concentration. This phenomenon might be attributed to the less availability to Cu(II) ions, and the similar results were also observed in Tang et al. (2012). Although the unit adsorption amount decreased as the increase of adsorbent dosage, the total adsorption amount (Cu(II) removal percentage) still increased along with the increase in dosage. From the trend shown in Fig. 2, it is rational to expect that as the dosage continuously increases, all the aqueous Cu(II) can be removed.

3.3. Adsorption kinetics

The variation in equilibrium concentration of Cu(II) with contact time at different initial Cu(II) concentrations is shown in Fig. 3.

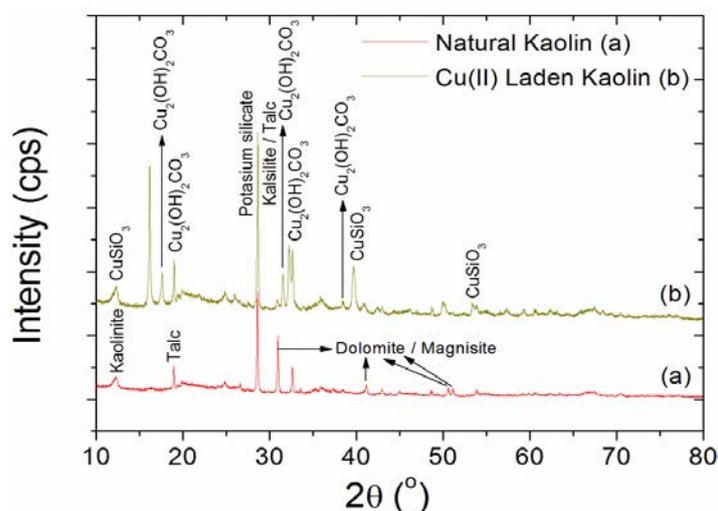


Fig. 1. XRD spectrum of natural Kaolin (a) and Cu(II) laden Kaolin (b)

The time to reach equilibrium was found to increase with increasing initial Cu(II) concentration.

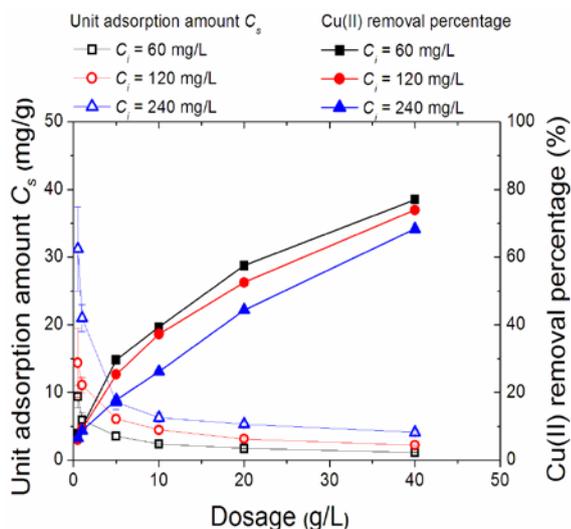


Fig. 2. Dosage effect on Cu(II) adsorption

The time to reach equilibrium is determined to be only around 48 h, when $C_i = 67$ mg/L, but it is to be expected that as initial Cu(II) concentration increases, more than 150 hours will be needed to reach adsorption equilibrium when $C_i = 134$ and 267 mg/L. In addition, following the initial rapid uptake, it was an ongoing slow adsorption process. The rapid stage is probably due to the abundant availability of active adsorption sites on the natural Kaolin, and with the gradual occupancy of these sites, the adsorption becomes less efficient in the slower stage.

Fig. 4 shows the variation in adsorption of adsorbent per gram with increasing contact time. From the chart, it is obvious that in the first 50 hours, the adsorption amount increased rapidly, but it seemed to maintain a constant C_s once a limit was reached. The time required to reach the adsorption equilibrium increased from 50 to 200 hours with increasing initial solute concentrations of 67 to 267 mg/L. In the chart, it can be observed that the unit adsorption amount at 182 hours was a little higher than that at 96 hours (25 mg/g). Thus, to reduce the experimental durations, reaction time of 96 hours was applied to most of the batch adsorption tests in this study.

The test data were further analyzed with three kinetic models (i.e., pseudo-first order kinetics, pseudo-second order kinetics and intraparticle diffusion model). The pseudo-first order kinetic equation can be written as Eq. (1) (Lagergren, 1898; Tang et al., 2012).

$$\lg(C_e - C_s) = \lg(C_e) - \frac{k_1}{2.303}t \quad (1)$$

where C_e and C_s are the amount of solute adsorbed per unit adsorbent at equilibrium and time point, respectively (mg/g), and k_1 is the pseudo-first order rate constant (h^{-1}).

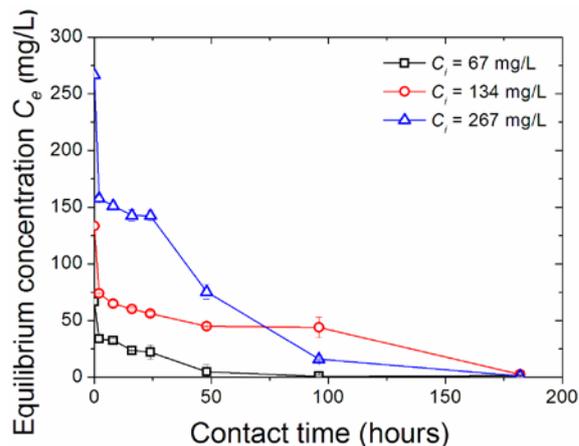


Fig. 3. Variation of equilibrium concentration of Cu(II) with contact time

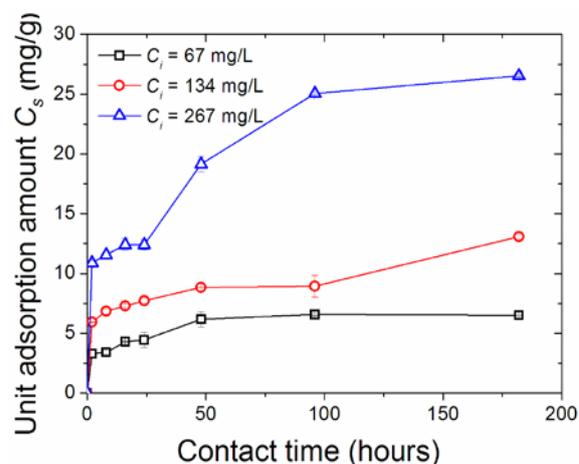


Fig. 4. Effect of contact time on the unit adsorption amount

The pseudo-second order kinetic equation is (Ho, 1995; Tang et al., 2012) (Eq. 2):

$$\frac{t}{C_s} = \frac{I}{k_2 C_e^2} + \frac{I}{C_e} t \quad (2)$$

where k_2 is the pseudo-second order rate constant ($\text{g/mg}\cdot\text{h}$). The equation on the intraparticle diffusion (Eq. 3) model is (Weber and Morris, 1963; Tang et al., 2012):

$$C_s = k_{int} t^{1/2} + C \quad (3)$$

where k_{int} is the relevant rate constant ($\text{mg/g}\cdot\text{h}^{1/2}$) and C is the intercept.

Table 2 lists the critical parameters of adsorption kinetics. From the correlation coefficient values listed in the table, we could easily judge that the pseudo-first order kinetics equation ($R^2 = 0.803, 0.732$ and 0.770) and the pseudo-second order kinetic equation ($R^2 = 0.884, 0.810$ and 0.823) could fit the test data well when initial concentration was not very high. The equation of the intraparticle diffusion model could be regarded as a good supplement when initial concentration was extremely high (i.e. $C_i = 134$ and 267 mg/L).

Table 2. Predicted kinetic constants of Cu(II) adsorption on natural Kaolin

C_i	Unit	67 mg/L	134 mg/L	267 mg/L
The pseudo-first order kinetics equation				
C_e	mg/g	6.158	8.871	24.994
k_1	h^{-1}	0.094	0.488	0.041
R^2		0.803	0.732	0.77
The pseudo-second order kinetic equation				
C_e	mg/g	6.387	9.9	27.39
k_2	$g/mg \cdot h$	0.032	0.04	0.002
R^2		0.884	0.81	0.823
The equation on the intraparticle diffusion model				
k_{int}	$mg/g \cdot h^{1/2}$	0.31	0.53	1.525
C		3.041	5.104	7.413
R^2		0.835	0.92	0.926

In addition, from the values listed in the chart, it is obvious that both k_1 and k_2 rose to the peak point value when the initial concentration reached 134 mg/L, as shown in results of the pseudo-first order kinetics and the pseudo-second order kinetic model (i.e. $k_1 = 0.488$, and $k_2 = 0.040$), which means that the system needs the least time to reach equilibrium when the initial concentration is neither very high nor low. However, the analysis with the intraparticle diffusion model shows that the rate constant k_{int} increased with increasing initial Cu(II) concentration. As the parameter k_{int} means the speed of inwards diffusion of soil particles, this process is governed by the gradient of solute at the interface between the soil and solution. The higher Cu(II) concentration gradient causes the higher diffusion rate, which is also consistent with Fick's diffusion law (Tang et al., 2014).

3.4. Isothermal adsorption

Fig. 5 shows the effect of temperature on Cu(II) removal efficiency. From this chart, higher temperature is found to lead to both increased unit adsorption amount and Cu(II) removal efficiency, obviously denoting the endothermic nature of Cu(II) adsorption on Kaolin. In addition, five isothermal equations were applied to evaluate the test results in order to uncover more information on adsorption mechanisms. The Langmuir isotherm can be written as (Do, 1998):

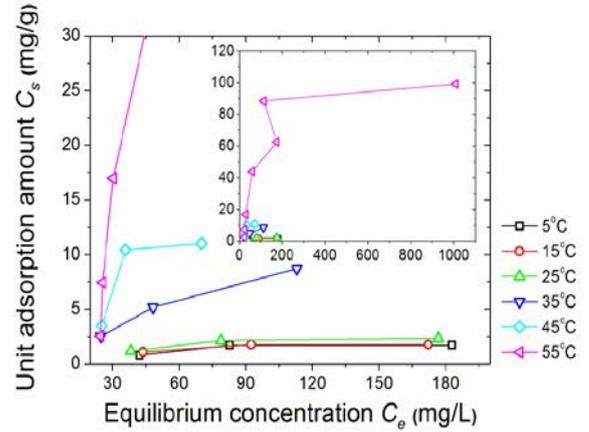
$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e} \quad (4)$$

where C_e is the equilibrium concentration of solute solution (mg/L), Q^0 the maximum adsorption capacity of the adsorbent (mg/g), and b (L/mg) the Langmuir constant.

The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, and characteristic of heterogeneous surfaces. The Freundlich isotherm can be expressed as:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant (mg/g) indicating the adsorption capacity and strength of the adsorptive bond, and n the heterogeneity factor. The values of R^2 are regarded as a measure of goodness-of-fit of experimental data to the isotherm models (Al-Asheh et al., 2000).


Fig. 5. Isothermal adsorption curves under different temperatures

The D-R model (Eq. 6) assumes a uniform pore-filling sorption and can predict the free sorption energy change by which the sorption type can be judged (Uslu and Tanyo, 2006). The D-R model is written as:

$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (6)$$

where q_m is the maximum adsorption capacity (mol/g), k is a model constant related to the free sorption energy and ε is the Polanyi potential, which is written as (Eq. 7):

$$\varepsilon = RT \ln(1 + (1/C_e)) \quad (7)$$

The mean free energy of adsorption (E) is Eq. (8):

$$E = -\frac{I}{\sqrt{2k}} \quad (8)$$

The adsorption is basically a surface adsorption associated with ion exchange when $|E|$ is between 8 and 16 kJ/mol. Otherwise, for $|E|$ ranging from 1.0 to 8.0 kJ/mol, the mechanism is physical adsorption (Romero-Gonzalez et al., 2005).

The Redlich-Peterson model is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations, and can be applied either in homogeneous or heterogeneous systems due to its versatility (Redlich and Peterson, 1959).

The Redlich-Peterson equation is expressed as Eq. (9):

$$q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^\beta} \quad (9)$$

where K_{RP} (L/g) and α_{RP} (L/mg) $^\beta$ are Redlich-Peterson model constants and β is the exponent which lies between 0 and 1.

Sips model is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems (Sips, 1948). At low concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption of Langmuir form (Eq. 10):

$$q_e = \frac{q_{mS}K_S C_e^{m_S}}{1 + K_S C_e^{m_S}} \quad (10)$$

where q_{mS} is the Sips maximum adsorption capacity (mg/g), K_S is the Sips equilibrium constant (L/mg) m_S , and m_S is the Sips model exponent.

Table 3 lists the predicted isothermal constants for Cu(II) adsorption on natural Kaolin. It is apparent that three-parameter models such as Redlich-Peterson model and Sips model fit test data better than two-parameter models based on the correlating coefficients. Most of the correlating coefficients in the Redlich-Peterson model and Sips model are higher than 0.9, which means the parameters could be measured more accurately through these two models. Especially for Sips model, the correlating coefficients are 0.99, 0.99, 0.99, 0.99, 0.99 and 0.93, which indicates Sips model fit best towards adsorption process.

According to Sips model results, the predicted Cu(II) adsorption capacities of natural Kaolin are found to increase from 1.72 to 1.78 and 3.00 mg/g with

increasing temperature from 278 to 288 and 298 K, respectively. The further increase in temperature from 298 to 308, 318 and 328 K led to a much sharper increase in adsorption capacity, which jumps from 3.00 to 11.28, 11.02 and 76.00 mg/g, respectively. This interesting and strange phenomenon has not been observed in other literature.

3.5. Effect of temperature and thermodynamics

For the sake of explaining the phenomenon referred to above, thermodynamic considerations must be introduced. Thermodynamic parameters such as enthalpy change (ΔH^0), Gibb's free energy change (ΔG^0) and entropy change (ΔS^0) can be estimated with the Gibb's free energy equations (Eqs. 11-13):

$$\Delta G^0 = -RT \ln K_D \quad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

where R is the universal gas constant (8.314 J/mol·K), T the absolute temperature (K) and K_D the partitioning coefficient in equilibrium (mL/g).

Values of ΔH^0 and ΔS^0 can be determined from the slope and the intercept of the plot of $\ln K_D$ versus $1/T$ (Aksu and Tunc, 2005; Tewari et al., 2005). The linearization of the test data based on Eq. (13), above, is as shown in Fig. 6. According to the slope and intercept, the predicted constants of thermodynamics can be calculated as shown in Table 4.

Table 3. Predicted constants of isothermal models for Cu(II) adsorption on natural Kaolin

Langmuir model	Unit	Temperature					
		278 K	288 K	298 K	308 K	318 K	328 K
Q^0	mg/g	2.44	2.30	3.15	21.00	24.58	117.68
b	L/mg	0.017	0.025	0.019	0.006	0.013	0.009
R^2		0.73	0.86	0.89	0.99	0.60	0.88
Freundlich model							
K_F	mg/g	0.24	0.38	0.36	0.29	0.70	12.43
n		2.57	3.25	2.70	1.38	1.51	3.54
R^2		0.63	0.76	0.80	0.98	0.57	0.73
D-R model							
q_m	mg/g	7.82	4.97	8.26	89.81	309.09	332.83
k	mol ² /kJ ²	0.007	0.004	0.005	0.008	0.009	0.007
E	kJ/mol	-8.45	-11.18	-10.00	-7.91	-7.45	-8.45
R^2		0.74	0.83	0.85	0.98	0.64	0.70
Redlich-Peterson model							
K_{RP}	L/g	0.041	0.057	0.061	0.133	0.312	1.032
α_{RP}	(L/mg) $^\beta$	0.017	0.025	0.019	0.006	0.013	0.009
β		1	1	1	1	1	1
R^2		0.92	0.98	0.97	0.99	0.84	0.86
Sips model							
q_{mS}	mg/g	1.72	1.78	3.00	11.28	11.02	76.00
K_S	(L/mg) m_S	2.7E-19	3.4E-9	1.0E-5	0.0017	3.5E-15	2.0E-5
m_S		11.38	5.29	3.09	1.61	10.09	2.70
R^2		0.99	0.99	0.99	0.99	0.99	0.93

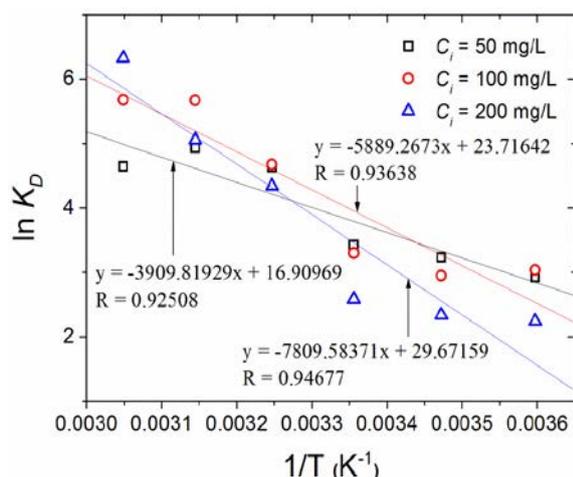


Fig. 6. Fitting test data with Gibb's free energy equations

Table 4. Thermodynamic parameters for adsorption of Cu(II) on Kaolin

C_i (mg/L)	Unit	50	100	200
Temperature		G	G	G
278 K	kJ/mol	-6.76	-7.01	-5.18
288 K	kJ/mol	-7.73	-7.06	-5.59
298 K	kJ/mol	-8.49	-8.17	-6.40
308 K	kJ/mol	-11.85	-11.98	-11.12
318 K	kJ/mol	-13.05	-15.00	-13.37
328 K	kJ/mol	-12.67	-15.48	-17.26
ΔS	J/mol·K	140.59	197.18	246.69
ΔH	kJ/mol	32.51	48.96	64.93
R		0.93	0.94	0.95

As shown in Table 4, the Gibb's free energy changes in Cu(II) adsorption with an initial concentration of 50 mg/L are found to range from -6.76, -7.73 and -8.49 to -11.85, -13.05 and -12.67 kJ/mol, respectively within the temperature range of 278 to 328 K. The same trend appears in conditions $C_i = 100$ and 200 mg/L, where the values of Gibb's free energy changes are approximately the same as the results of Lin and Juang (2002), suggesting a spontaneous adsorption process which could be enhanced by the increasing temperature. Because the correlation coefficients between the fitted curve of thermodynamic function and the test data are 0.925, 0.936 and 0.947 for Cu(II) adsorption on Kaolin with initial Cu(II) concentration ranging from 50 to 100 and 200 mg/L, respectively, the Gibb's free energy equations fit the test data well. The enthalpy changes of Cu(II) adsorption on the natural Kaolin are predicted to be 32.51, 48.96 and 64.93 kJ/mol while the entropy changes are 140.59, 197.18 and 246.69 J/mol·K for solutions with initial Cu(II) concentrations of 50, 100 and 200 mg/L, respectively. In addition, the value of adsorption enthalpy change extrapolated in this study is close to the 39.52 kJ/mol described by Yavuz et al. (2003). The adsorption of Cu(II) could be viewed as an endothermic and preferential process, while the adsorption affinity appeared to be increased with the increasing solute concentration because of the

increasing of entropy change. This might be the reason for the rapid increase in Cu(II) adsorption capacity with increasing temperature.

In addition, the free adsorption energies at 278, 288, 298, 308, 318 and 328 K were determined to be fluctuating around -10 kJ/mol by the D-R model with $R^2 > 0.7$. These values are close to the predicted Gibb's free energies shown in Table 4, confirming the spontaneous adsorption process in ion exchange form.

3.6. Effect of pH

Fig. 7 plots the percentage of Cu(II) adsorption on Kaolin versus the initial solution pH (pH_i). From this figure it is obvious that the solution pH had a significant effect on Cu(II) adsorption on natural Kaolin. A sharp increase can be observed between pH 6.0 and 7.3. Before the significant increase in Cu(II) adsorption percentage occurred, the adsorbed Cu(II) increased gradually from 34.3 % to 42.6 % with increasing pH from 3.38 to 6.01. The increase in pH_i from 7.92 to 10.01 led to only 1 % more Cu(II) removal. In addition, there appeared to be a decrease in Cu(II) adsorption from 90 % to 83.7 % at $pH > 8.93$ which might be caused by dissolution of immobilized Cu(II) in alkaline solutions.

Fig. 8 shows the variation in equilibrium pH (pH_e) under different initial pH solutions (pH_i). From the chart, it can be easily observed that at $pH_i < 6.0$, the pH_e was found to be higher than pH_i after equilibration. When $pH_i \geq 9.0$, the pH_e became lower than pH_i . But with $6.0 < pH < 9.0$, the pH_e was equal to pH_i (pH remained between 6.0 and 6.2), as shown in Fig. 8. It is obvious that the natural Kaolin has good buffering capability which can resist pH changes effectively, especially for acidic solutions with $pH < 6.01$. This effect failed in solutions with $pH > 6.0$. The changing pattern of pH_e might reflect the inherent mechanism that governs the adsorption of Cu(II) on Kaolin, particularly regarding the effect of the pH of the solution.

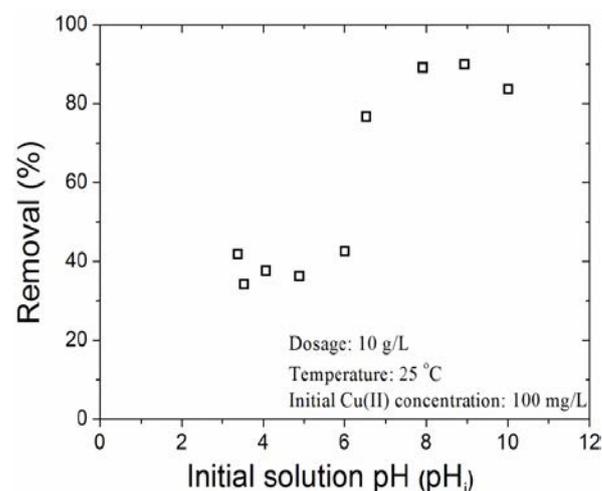


Fig. 7. Effect of pH on adsorption edge of Cu(II) on natural Kaolin

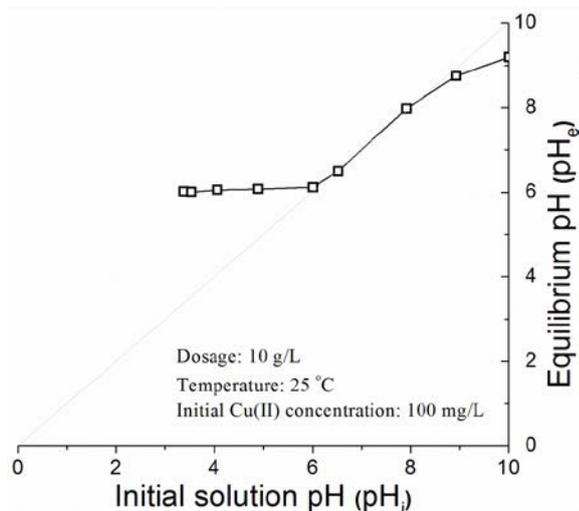
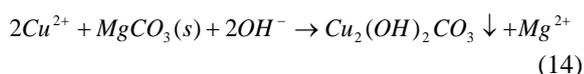


Fig. 8. Variation in equilibrium pH (pH_e) under different initial solution pH (pH_i)

4. Discussions of adsorption mechanism

This paper dealt with the adsorption behavior of Cu(II) on natural Kaolin. The results indicate that various factors have a significant effect on the adsorption process, i.e. mineral component, pH, temperature, initial Cu(II) concentration and duration, among which, the mineral component, reaction temperature and pH appeared to be most significant.

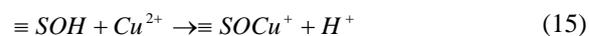
The pattern (b) shown in Fig. 1 was the XRD pattern of natural Kaolin with Cu(II) loading. By contrasting patterns (a) and (b), it can be determined that the bands related to white mica and magnesium carbonate (Dolomite and Magnesite) in natural Kaolin disappeared after adsorption with Cu(II), while new bands corresponding to new substances appeared ($Cu_2(OH)_2CO_3$ and $CuSiO_3$ (copper silicate)). More precisely, the appearance of $Cu_2(OH)_2CO_3$ indicates the following reaction (Eq. 14):



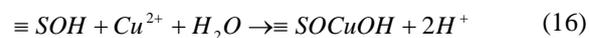
The reaction shown in Eq. (14) might be a slow process since the time to reach equilibrium was greater than 96 hours, as shown in Fig. 3. The formation of $Cu_2(OH)_2CO_3$ would cover the surface of the reagent (magnesium carbonate) and thus prevent the further reaction from occurring. This phenomenon could also explain why the kinetic constants k_1 and k_2 decreased gradually with increasing initial Cu(II) concentration when the initial Cu(II) concentration was > 134 mg/L, as shown in Table 2.

In addition, the existence of $CuSiO_3$ (copper silicate) demonstrates that Kaolinite, as the main constituent of natural Kaolin, also contributes to Cu(II) adsorption. The mechanism of Cu(II) adsorption on carbonate greatly differs from that on Kaolinite. The former could be viewed as an ion exchange process. The presence of a great quantity of $Cu_2(OH)_2CO_3$ confirmed this speculation as well as

that which resulted from the D-R model. The latter was most likely to be a surface complexation process. Du et al. (1997) have reported the adsorption of Cu(II) on Illite and suggested the following adsorptions (Eqs. 15-16):



and

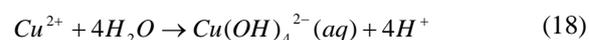
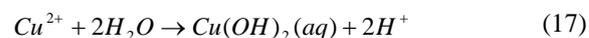


where $\equiv S$ represents the silicate contained in clay minerals. Other researchers have confirmed the presence of surface complexes, as shown in Eq. (15) and Eq. (16) in Cu(II) loaded Kaolinite (Alvarez-Puebla et al., 2005; Peacock and Sherman, 2005). The adsorption of metals on clay often involves a chemical reaction between surface functional groups and the metal ions, thus forming metal-inorganic complexes, or a cation-exchange reaction due to high cation-exchange capacity of the adsorbent (Ho et al., 2001). This corresponds to our own speculation.

Heavy metals like Cu(II) could be adsorbed on Kaolinite via two major mechanisms: edge adsorption, and cleavage plane surface adsorption (Stadler and Schindler, 1993). Because of the crystal lattice defects, overall charge on the edge of the particles becomes negative in most cases but depends on the pH of the solution. The charge on the basal faces of the Kaolinite particles, which belong to strong adsorption sites, is permanently negative and independent of solution pH change (Alkana et al., 2008). The crystal edge of Kaolin mineral crystal is an aluminium hydroxide bond and the charges will change along with the pH of solution, known as the variable charge sites. These can be combined in the form of outer-sphere complexes (Srivastava et al., 2005).

The percentage adsorption of Cu(II) is shown in Fig. 7 as a function of pH. When the pH of the solution was as low as 3.38, about 35% of Cu(II) had been removed, and when the pH reached 8.75, Cu(II) adsorption percentage peaked (90.0%). It is to be expected that with further increases in pH, the percentage removal of Cu(II) will decrease gradually because of dissolution of immobilized Cu(II). In addition, according to variation in pH_e versus pH_i plotted in Fig. 8, when pH_i was regulated at a high level, pH_e will always be lower than pH_i since the OH^- is involved in formation of Cu(II) precipitates ($Cu_2(OH)_2CO_3$).

Kalbe et al. (2008) and Tang et al. (2015) attributed the Cu precipitate transformation to free Cu(II) at high pH levels to the amphoteric character of most heavy metals. Cu(II) is soluble at low pH values as a Cu^{2+} or $CuCl^+$ ion, and as a hydroxy-complex at higher pH values, as shown below (Eqs. 17-18):



In addition, in the presence of complexing ligands such as Cl^- or CO_3^{2-} , other complexes are possible (Kalbe et al., 2008; Tang et al., 2015). Thus considering the pH conditions and the presence of CO_3^{2-} , it was rational to expect the heavy metals to be dissolved again, as shown in Fig. 7.

Table 5 shows some reported data about Cu(II) adsorption capacities by different adsorbents. Compared with other adsorbents, the natural Kaolin used in this study has the higher adsorption capacity. The advantage of usage of natural Kaolin towards Cu(II) lies in: 1) utilization of “valueless” material; 2) ease in preparation process; 3) strong affinity towards Cu(II) especially under condition of high temperature; 4) abundant adsorption sites etc., and thus appears promising in the treatment of wastewaters.

Table 5. Reported Cu(II) adsorption capacity of various adsorbents

	Adsorbent	Cu(II) sorption capacity (mg/g)	Reference
1	Rice husk	29	Wong et al. (2003)
2	Banana pith	13.46	Low et al. (1995)
3	Sugar beet pulp	28.5	Aksu and Isoglu (2005)
4	Papaya wood	19.88	Saeed et al. (2005)
5	Olive stone waste	2.04	Fiol et al. (2006)
6	This study	76	

5. Conclusions

(1) The natural Kaolin studied in this paper appeared to be predominant in Cu(II) removal from aqueous solution and exhibited promising potential for application in industry, since the adsorption capacity towards Cu(II) was determined 76 mg/g.

(2) When initial Cu(II) concentration was raised from 67 to 267 mg/L, the time to reach equilibrium was prolonged to over 150 hours from 50 hours.

(3) The kinetics data are well fitted with the pseudo-first order kinetics equation and the pseudo-second order kinetic equation at lower initial concentrations ($C_i = 67$ mg/L). The intraparticle diffusion model appeared to be satisfactory at higher initial Cu(II) concentrations (134 and 267 mg/L).

(4) The three-parameter models fits test data better than the two-parameter models and can demonstrate the character of the adsorption process better. Sips model fit the test data best, in which the correlating coefficients in the Sips model are greater than 0.93.

(5) The adsorption of Cu(II) on Kaolin could be viewed as an endothermic reaction and a preferential process, with an enthalpy change of around 50 kJ/mol. The negative Gibb's free energy changes (ranging from -6.76, -7.73 and -8.49 to -11.85, -13.05 and -12.67 kJ/mol) indicate a spontaneous adsorption procedure.

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