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Thermodynamics, isotherm and kinetics for adsorption of Cu(II) onto Na-bentonite

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ABSTRACT

The adsorption characteristic of low Cu(II) concentration onto Na-bentonite as an adsorbent as a function of pH, dosage of Na-bentonite, temperature, initial Cu(II) concentration and contact time was systematically studied using batch technique. In order to reveal the adsorption characteristic of Na-bentonite, surface area, total pore volume, mean pore diameter, IR, XRD, DTA and TG were carried out. Graphical correlation of various adsorption isotherm models like Langmuir and Freundlich have been investigated for Na-bentonite. The thermodynamic parameters such as variation of enthalpy, variation of entropy and variation of Gibbs free energy were calculated. The pseudo-first-order, pseudo-second-order, parabolic diffusion and Elovich models were used to fit the adsorption kinetics. The result showed Na-bentonite was suitable as a low cost adsorbent for removal of Cu(II) from aqueous solutions.

Keywords: Adsorption; Na-bentonite; Cu(II); Isotherm; Kinetics; Thermodynamics

1. Introduction

Copper is one of the common and toxic heavy metals released into natural waters from several industries such as the electroplating industry and refineries [1]. It is obvious that excessive copper would bring harm to human beings and environment.

The common methods for Cu(II) removal from wastewater include membrane systems, precipitation and adsorption [2,3]. Among the methods adsorption systems are more effective and economical in reducing Cu(II) concentration. At present, kinds of adsorbents for example, activated carbon, resin, synthetic zeolite, clay mineral etc., have been investigated for Cu(II) removal from wastewaters [4,5]. However the use of activated carbon, resin and synthetic zeolite are not suitable for developing countries due to their high manufacturing costs. Thus clay mineral with large quantities, high specific surface area, chemical stability and structural properties has great potential as inexpensive and efficient adsorbents for the treatment of Cu(II) from industrial wastewater. Bentonite, a representative clay mineral, mainly contains montmorillonite which is a 2:1-type aluminosilicate. The inner layer is built up of an aluminum oxide octahedral sheet situated between two silicon oxide tetrahedral sheets. Substitutions within the lattice structure of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminium in the octahedral sheet result in a net negative charge on the clay surfaces. The charge imbalance is made up by exchangeable cations such as H^+, Na^+, K^+, Mg^{2+} or Ca^{2+} on the layer surfaces [6].

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Bentonite is usually classified into sodium (Na-bentonite) or calcium (Ca-bentonite) types owing to dominant exchangeable ion. Na-bentonite with the most suitable physico/chemical properties has been used as the best backfill material in the disposal of radioactive nuclear waste [7]. Mineralogical and geotechnical investigations on the possible use of compacted bentonite as a buffer material in nuclear waste repositories are reported [8]. It is significant to investigate the adsorption characteristic of Na-bentonite because the Na-bentonite resource is abundant worldwide [9]. The dependence of metal adsorption on the adsorbent can be associated with experimental conditions.

The aim of this study was to systematically investigate the possible use of Na-bentonite as an adsorbent for the removal of Cu(II) from aqueous solution. The adsorption of low Cu(II) concentration onto Na-bentonite was studied by varying experimental conditions and then the experimental data fitted using different adsorption thermodynamics, isotherm and kinetics model.

2. Experimental

2.1. Materials

The sample of Na-bentonite from Gaomiaozi Country (Inner Mongolia Autonomous Region, China) was sieved from no. 120 sieve to obtain finer grains, dried in an oven at 105°C for a period of 24 h, and then stored in a desiccator. The N_2-BET surface area of the sample particles was 28.82 $m^2\ g^{-1}$. The total pore volume and mean pore diameter were up to 0.072 $cm^3\ g^{-1}$ and 2.3132 nm, respectively. The cation exchange capacity (CEC) was 74.05 mmol/100 g by using the ammonium acetate method. The physicochemical properties of Na-bentontie were determined by using X-ray diffractometer (XRD), infrared (IR), thermogravimetry (TG) and differential thermal analysis (DTA). The X-ray powder diffraction pattern of Na-bentonite crystal was recorded on Lab X XRD-6100 XRD (Shimadzu) and performed with CuKα radiation ($\lambda = 0.1541$ nm). The 2θ-scanning rate was 2 min^{-1}. XRD pattern indicated that the dominating composition of Na-bentonite was montmorillonite with a layer of crystal water [10]. The Fourier transform infrared (FTIR) spectrum of Na-bentonite was characterized using Thermo Nicolet AVATAR 360 FTIR (America) in pressed KBr pellets (0.4 mg of sample and 200 mg of KBr). The spectral resolution was set to 4 cm^{-1}, and 64 scans were collected for each spectrum. In IR spectrum, the adsorption peaks at 524 and 468 cm^{-1} corresponded to Si-O-Al and Si-O-Fe bending vibrations in the montmorillonite lattice skeleton [10]. The TG and DTA curves were obtained simultaneously using DTG-60H Thermal Analyzer (Shimadzu). The measurements were carried out in flowing nitrogen atmosphere with a flow rate of 50 ml min^{-1}. The heating rates were 10°C min^{-1} and the sampling masses were in the range of 10–20 mg. The three endothermal valleys shown in TG and DTA patterns were the characteristic endothermal valleys of Natrium-montmorillonite. It indicated bentonite used in experiments was Na-bentonite. The chemical compositions of bentonite are SiO_2 69.17%, Al_2O_3 14.43%, Fe_2O_3 3.12%, FeO 0.02%, Na_2O 1.95%, K_2O 0.83%, CaO 1.29%, MgO 3.31%, MnO 0.04% and TiO_2 0.13%. The $(Na^{+}K)/Ca$ is 2.2. It also shows that the high-silica montmorillonite are enriched with sodium and potassium [10].

All chemicals used in experiments were of analytical grade. Stock solution of Cu(II) ions was prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (Shanghai Chemical Reagents Ltd.) and diluted as required. Water used was deionized.

2.2. Adsorption procedures

Adsorption studies were carried out by batch technique. The conical flasks with screw cap were filled with a given dosage of Na-bentonite and a given volume of Cu(II) ion solution of different concentrations. The pH of the solution was adjusted with negligible volumes of 0.10 mol l^{-1} HNO_3 or NaOH. The suspensions were shaken for a reasonable time at constant temperatures and oscillation frequencies. Then the suspension was centrifuged to separate solid and liquid phases by a centrifugation at 7000 rpm for 30 min. The concentration of Cu(II) in the supernatant was determined by using an atomic absorption spectrometer. The flame type was air-acetylene and the absorption wavelength was 324.8 nm for Cu(II). The adsorption percentage (D%) and distribution coefficient (K_d l g^{-1}) were calculated by following equations:

$$D = \frac{C_i - C_e}{C_i} \times 100\% \tag{1}$$

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} = \frac{Q_e}{C_e} \tag{2}$$

where C_i is the initial concentration and C_e is the equilibrium concentration of Cu(II) (mg l^{-1}); Q_e is the equilibrium adsorption capacity (mg g^{-1}); V is the volume of the solution (l) and m is the dosage of the Na-bentonite (g). All experimental data were the average of duplicate. Measurements were, in general, reproducible within ±10%.

3. Results and discussion

3.1. Effect of dosage of Na-bentonite

The adsorption of Cu(II) onto Na-bentonite as a function of dosage of Na-bentonite is shown in Fig. 1. It can be proved that the adsorption percentage of Cu(II) increases as the dosage of Na-bentonite increases. Because dosage

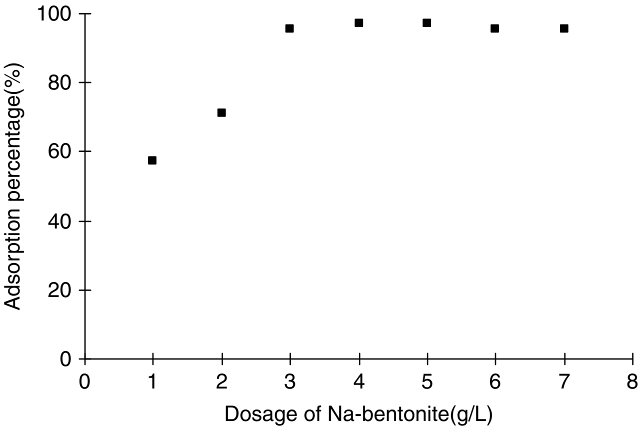

Fig. 1. Effect of dosage on the adsorption of Cu(II) onto Na-bentonite. $C_{\mathrm{Cu(II)}}$ = 30 mg l^{-1}, pH = 5, T = 298 K, contact time 1 h and oscillating frequency 300 rpm.

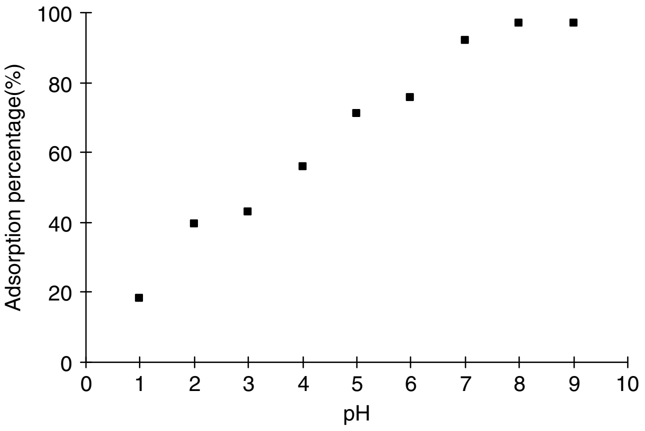

Fig. 2. Effect of pH on the adsorption of Cu(II) onto Na-bentonite. $C_{\mathrm{Cu(II)}}$ = 30 mg l^{-1}, m/V = 2 g l^{-1}, T = 298 K, contact time 1 h and oscillating frequency 300 rpm.

of Na-bentonite increases, a lot of functional groups available sites for binding Cu(II) increase. More sites enhance the formation of complexation between Cu(II) and Na-bentonite and more exchangeble cations would favor for Cu(II). Similar results have been reported [11]. It is noted that K_d value increases as the dosage of Na-bentonite increases from 1 to 4 g l^{-1}, then decreases drastically as the dosage of Na-bentonite increases from 4 to 7 g l^{-1}. The effective adsorption sites do not increase as the dosage of Na-bentonite increases. This can be explained that the more dosage of Na-bentonite becomes such a gel-like sticky material by interaction with water and the sticky Na-bentonite blocks some the adsorption sites from the adsorbing solutes. Xu et al. [12] explained that the competition among the functional groups decreases the adsorption and complexation ability of bentonite.

3.2. Effect of pH

Fig. 2 shows the pH dependence of Cu(II) adsorption onto Na-bentonite. It is clear that pH of the solution plays an important role in the adsorption of heavy metal ions onto bentonite [13,14]. It can be seen from Fig. 2 that the adsorption percentage increases from 18.44% to 97.08% with the increase of pH from 1 to 9. The adsorption edges can be divided into two regions. From pH 1 to 7, the adsorption of Cu(II) on Na-bentonite increases sharply. From pH 7 to 9, the adsorption of Cu(II) remains unchanged. In principle, the dependence of metal adsorption on pH can be associated with both the surface functional groups on the adsorbent as well as the metal chemistry of the solution [15]. Cu(II) present in the forms of Cu^{2+}, $Cu(OH)^{+}$, $Cu_2(OH)_2^{2+}$, $Cu(OH)_2^{0}$, $Cu(OH)_3^{-}$ and $Cu(OH)_4^{2-}$ at various pH values. Cu(II) is adsorbed onto Na-bentonite mainly via two different ways: Cu(II) mainly exchanges with Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} etc., in the inter-layers below pH 7, while above pH 7 Cu(II) forms inner-sphere complexes with Si-O^{-} and Al-O^{-} groups at the Na-bentonite particle edges or $Cu(OH)_2$ precipitates [16].

3.3. Effect of initial concentration and adsorption isotherm

As it is showed in Fig. 3, the adsorption percentage decreases as the initial Cu(II) concentration increases from 10 to 80 mg l^{-1}. Langmuir and Freundlich are often applied to deeply investigate the mechanism of adsorption [17]. The linear forms of the adsorption isotherm models have been expressed as follows:

The linear form of the Langmuir model:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{3}$$

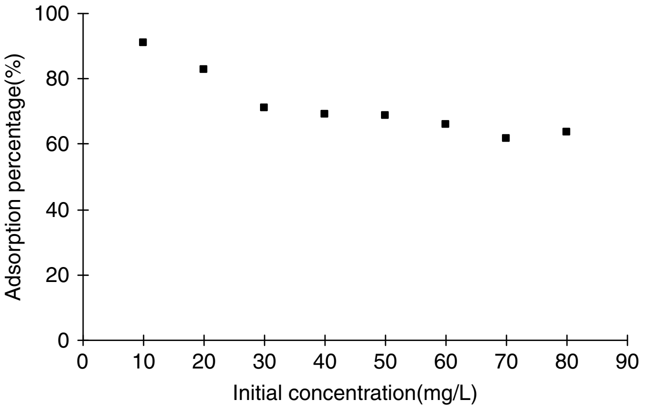

Fig. 3. Effect of initial concentration on the adsorption of Cu(II) onto Na-bentonite. m/V = 2 g l^{-1}, pH = 5, T = 298 K, contact time 1 h, oscillating frequency 300 rpm.

Table 1
Isotherm parameters of the adsorption of Cu(II) onto Na-bentonite

Metal ion	Langmuir			Freundlich		
	Q_{max}(mg g^{-1})	K_L	R^2	$1/n$	K_F	R^2
Cu(II)	26.1643	0.2664	0.9701	2.6693	7.1506	0.8441

The linear form of the Freundlich model:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{4}$$

where Q_e is the equilibrium concentration of Cu(II) onto the adsorbent (mg g^{-1}), Q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir constant and related to the free energy of adsorption; K_F is Freundlich constant in connection with adsorption capacity and n (dimensionless) is the heterogeneity factor.

The plots of C_e/Q_e versus C_e (Langmuir) and lgC_e versus lgQ_e for the adsorption of Cu(II) onto Na-bentonite were fitted and the relevant parameters have been shown in Table 1.

It is shown from Table 1 that the correlation coefficient (R^2) of Langmuir is better than that of Freundlich. Thus the adsorption of Cu(II) onto Na-bentonite could be better described by Langmuir model rather than Freundlich model. Freundlich model is used to describe the adsorption of solutes from a liquid to a solid surface. And Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption happens in a monolayer [18]. Moreover Na-bentonite has a limited adsorption capacity, thus the adsorption could be better described by the Langmuir model rather than by the Freundlich model. The maximum adsorption capacity (Q_{max}) of Cu(II) onto Na-bentonite calculated from Langmuir isotherm equation is 26.16 mg g^{-1}. The maximum adsorption capacity of Cu(II) onto Na-bentonite is consistent with values from other reports [19,20].

3.4. *Effect of temperature and thermodynamic*

As it is shown in Fig. 4, the adsorption percentage increase as temperature increases from 303 to 333 K. Thermodynamics parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) can be determined from the temperature dependence and calculated by using the following equations [21,22]:

$$\Delta G = -RT \ln K_d \tag{5}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

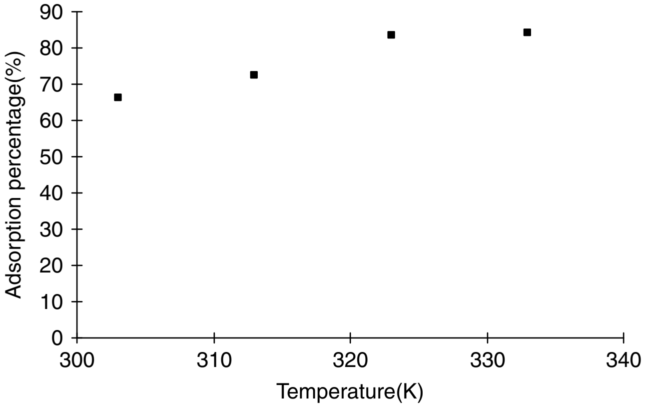

Fig. 4. Effect of temperature on the adsorption of Cu(II) onto Na-bentonite. $C_{Cu(II)}$ = 30 mg l^{-1}, m/V = 2 g l^{-1}, pH = 5, contact time 1 h, oscillating frequency 300 rpm.

where R (8.3145 J mol^{-1} K^{-1}) is the gas constant and T is the temperature in Kelvin; ΔG, ΔH and ΔS are free energy change (kJ mol^{-1}), enthalpy change (kJ mol^{-1}) and entropy change (J mol^{-1} K^{-1}), respectively.

The values of thermodynamic parameters for the adsorption of Cu(II) onto Na-bentonite have been tabulated in Table 2. The positive value of enthalpy change illustrates that the adsorption of Cu(II) onto Na-bentonite is an endothermic process. The temperature increases, the adsorption percentage increases. This may be explained that Cu(II) with a high hydration is hardly solvated in water, requires decomposition of its hydration shell for adsorption onto Na-bentonite. The adsorption process requires energy. It can be inferred that the adsorption of Cu(II) onto Na-bentonite is a chemical adsorption process because of endothermic character. The positive value of entropy, which illustrates that the adsorption process is

Table 2
Thermodynamic parameters of the adsorption of Cu(II) onto Na-bentonite

Metal ion	ΔH(kJ mol^{-1})	ΔS(J mol^{-1} K^{-1})	ΔG(kJ mol^{-1})	T(K)
Cu(II)	26.68	90.41	–0.70	303
			–1.45	313
			–2.95	323
			–3.19	333

irreversible, reflects the affinity of Na-bentonite toward Cu(II) in aqueous solutions and suggests some structure changes in the adsorbent. The value of ΔG becomes more negative with an increase of temperature. The result shows that the adsorption is a spontaneous process and more favorable at higher temperature [23–25]. At high temperature Cu(II) is readily desolvated and hence its adsorption becomes more favorable [26].

3.5. Effect of contact time and kinetics

The effect of contact time on the adsorption of Cu(II) onto Na-bentonite is shown in Fig. 5. It is easily seen that the adsorption percentage and K_d increase with increasing contact time and then reach their maximum values. Many effect of contact time on the adsorption of Cu(II) onto Na-bentonite have been investigated [19,20]. But it is interesting and seldom reported that the oscillating frequency strongly affects the equilibrium time for adsorption. Different oscillating frequencies result in different equilibrium time and equilibrium concentration in solution: 170 rpm for 90 min and 15.95 mg l^{-1}, and 300 rpm for 15 min and 7.22 mg l^{-1} in this study. This may attribute to that the liquid membrane thickness decreases, as the oscillating frequency increases.

Four kinetic models of pseudo-first-order, pseudo-second-order, parabolic diffusion and Elovich have been used to analyze the adsorption of Cu(II) onto Na-bentonite. Four equations corresponded to the kinetic models have been given as follows:

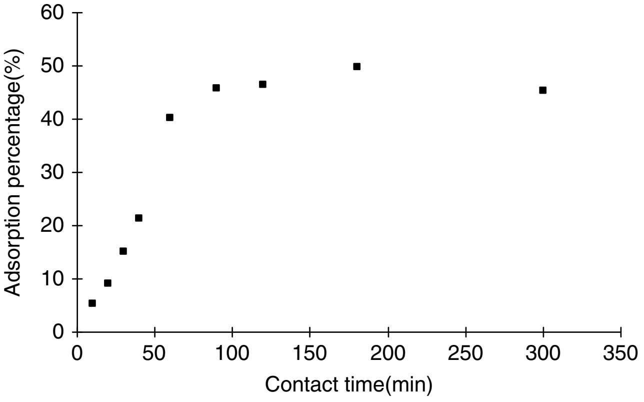

Fig. 5. Effect of contact time on the adsorption of Cu(II) onto Na-bentonite. $C_{\mathrm{Cu(II)}} = 30$ mg l^{-1}, $T = 298$ K, $m/V = 2$ g l^{-1}, pH = 5, oscillating frequency 170 rpm.

The equation of the pseudo-first-order model:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \qquad (7)$$

The equation of the pseudo-second-order model:

$$\frac{t}{Q_t} = \frac{1}{Q_{e2}^2 k_2} + \frac{t}{Q_{e2}} \qquad (8)$$

The equation of parabolic diffusion model:

$$Q_t = a_p + b_p t^{1/2} \qquad (9)$$

The equation of Elovich model:

$$Q_t = a_e + b_e \ln t \qquad (10)$$

where Q_{e1} and Q_t are the equilibrium amount of Cu(II) adsorbed onto Na-bentonite (mg g^{-1}) and the amount at various time t (mg g^{-1}); k_1 is the rate constant of the pseudo-first-order model for the adsorption process ($\min^{-1}$); Q_{e2} is equilibrium adsorption capacity (mg g^{-1}) and k_2 is the rate constant for the pseudo-second-order model (g mg^{-1} min^{-1}); a_p, a_e and b_e are constants and b_p represents the rate coefficient.

The straight-line plots of $\log(Q_{e1} - Q_t)$ versus $1/t$ for the pseudo-first-order model, t/Q_t against t for the pseudo-second-order model, Q_t against $t^{1/2}$ for the parabolic diffusion model and Q_t versus $\ln t$ for the Elovich model have been drawn to obtain kinetic parameters listed in Table 3.

The correlation coefficient (R^2) and F-test of the pseudo-second-order model is better than those of other three models. It is possible that the adsorption behaviour of Cu(II) on Na-bentonite follow the pseudo-second-order models. The chemical adsorption rather than physical adsorption is the rate controlling mechanism. Ion exchange and inner-sphere complexation may contribute to the adsorption of Cu(II) onto Na-bentonite.

Table 3
Kinetic parameters of the adsorption of Cu(II) onto Na-bentonite

Pseudo-first-order			Pseudo-second-order			Parabolic diffusion equation			Elovich		
Q_{e1}	k_1	R^2 (F^a)	Q_{e2}	k_2	R^2 (F^a)	a_p	b_p	R^2 (F^a)	a_e	b_e	R^2 (F^a)
23.53	267.8	0.9837 (269.3)	9.510	1.38×10^{-3}	0.9849 (291.2)	0.2880	0.4997	0.7224 (13.31)	−4.705	2.294	0.8620 (26.03)

[a] $F_{0.05}$ (1,9–2) = 5.59.

4. Conclusions

The mesoporous Gaomiaozi Na-bentonite was characterized using XRD, IR, DTA, TG and BET. The increase of dosage of Na-bentonite and pH are favorable for the Cu(II) adsorption. The adsorption process agreed very well with Langmuir model. The thermodynamic parameters exhibit that the adsorption of Cu(II) onto Na-bentonite is a spontaneous, endothermic and entropy increment process. The adsorption followed a pseudo-second-order kinetic model well, indicating that chemical adsorption is the rate-limiting step. The experimental results show that Na-bentonite could be used for the adsorption of Cu(II) from aqueous solutions.

Acknowledgements

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