Removal of copper ions from aqueous solution by adsorption using LABORATORIES-modified bentonite (organo-bentonite)

by Aning Ayucitra

RESEARCH ARTICLE

Removal of copper ions from aqueous solution by adsorption using LABORATORIES-modified bentonite (organo-bentonite)

Sandy[1], Velycia MARAMIS[1], Alfin KURNIAWAN[1], Aning AYUCITRA[1], Jaka SUNARSO[2],
Suryadi ISMADJI (✉)[1]

1 Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Surabaya 60114, Indonesia
2 Australian Research Council (ARC) Centre of Excellence for Electromaterials Science,
Institute for Technology Research and Innovation, Deakin University, Victoria 3125, Australia

Abstract Equilibrium, kinetic and thermodynamic aspects of the adsorption of copper ions from an aqueous solution using linear alkylbenzene sulfonate (LABORATORIES) modified bentonite (organo-bentonite) are reported. Modification of bentonite was performed via microwave heating with a concentration of LABORATORIES surfactant equivalent to 1.5 times that of the cation exchange capacity (CEC) of the raw bentonite. Experimental parameters affecting the adsorption process such as pH, contact time and temperature were studied. Several adsorption equations (e.g., Langmuir, Freundlich, Sips and Toth) with temperature dependency were used to correlate the equilibrium data. These models were evaluated based on the theoretical justifications of each isotherm parameter. The Sips model had the best fit for the adsorption of copper ions onto organo-bentonite. For the kinetic data, the pseudo-second order model was superior to the pseudo-first order model. Thermodynamically, the adsorption of copper ions occurs via chemisorption and the process is endothermic ($\Delta H^0 > 0$), irreversible ($\Delta S^0 > 0$) and nonspontaneous ($\Delta G^0 > 0$).

Keywords heavy metal, copper, adsorption, organo-bentonite, temperature dependent

1 Introduction

The removal of heavy metals from contaminated effluents is a matter of great interest in the field of environmental restoration, especially in this era of environmentally sustainability. Copper is a heavy metal commonly found in wastewater which primarily originates from the pipeline

exhausts of metallurgical, electroplating, printing circuits, fertilizer and refining industries. Generally, the concentration limit for Cu(II) ions in effluents to be discharged directly into in-land surface water is 3.0 mg/L whereas in drinking water the limit is 0.05 mg/L [1]. Despite the beneficial effects of trace amounts (µg/L) of copper for promoting the enzymatic activities of some microorganisms, high concentrations of this metal ion are undesirable since they cause irreversible inhibition of some enzymes [2]. Moreover, the prolonged oral administration of excess quantities of copper ions to humans may cause liver damage and acute poisoning.

Several conventional methods are available for the treatment of effluents containing copper ions such as precipitation, chemical oxidation, ion exchange, reverse osmosis, membrane filtration and electrochemical treatment [3]. However, most of these methods are ineffective for removing low concentrations ($\leqslant 10$ mg/L) of metal ions and result in toxic sludge production which requires extra cost for treatment and disposal [4]. On the other hand, adsorption is known as a cost effective and promising physiochemical process for this purpose. Numerous studies on the removal of Cu(II) ions from wastewater or aqueous solutions by adsorption using different kinds of adsorbents have been reported [2,5–7]. To this end, clays and clay minerals have emerged as alternative and inexpensive adsorbents featuring high specific surface areas and high cation exchange capacities as well as good mechanical and chemical stability [8].

The objective of this work was to evaluate various equilibrium, kinetic and thermodynamic aspects of the adsorption of Cu(II) ions from an aqueous solution using linear alkylbenzene sulfonate (LABORATORIES) modified bentonite (organo-bentonite). Temperature dependent forms of the Langmuir, Freundlich, Sips and Toth equations were used to correlate adsorption equilibrium

data at various temperatures. Up until now, few studies have reported the application of these equations to adsorption equilibrium data, especially for metal ions. Most studies on the adsorption of metal ions from wastewater or aqueous solutions have used adsorption equations without temperature dependency to correlate adsorption equilibrium data at various temperatures [9–12]. Recently, several adsorption equations with temperature dependency were employed to evaluate the equilibrium data of dye and antibiotic compounds [13,14].

2   Materials and methods

2.1   Materials

The bentonite was Ca-bentonite and collected from a mining site in Ponorogo, East Java, Indonesia. Prior to modification, the bentonite was crushed into powder with a micro-hammer mill (JANKE and KUNKEL) and sieved through a 100/120 mesh screen. The powder was then dried in an oven at 105°C for 2 h. The cation exchange capacity (CEC) of the bentonite powder was 0.55 meq/g clay according to ASTM C837-99 procedure. Elemental analysis of bentonite was performed with an atomic absorption spectrophotometer (Shimadzu AA6200) with the results as follow: Al_2O_3 30.71%, SiO_2 48.22%, FeO 3.14%, CaO 3.76%, MgO 0.56%, K_2O 0.17%, Na_2O 1.42% and MnO 0.4%.

An analytical grade of linear alkylbenzene sulfonate (LABORATORIES) surfactant was purchased from Merck and used as the modifying agent in the organo-bentonite preparation. Copper sulfate ($CuSO_4·5H_2O$; A.R. Grade; Sigma Aldrich) was used as the metal ion source.

2.2   Preparation of organo-bentonite

The organo-bentonite was prepared by the following procedure: 20 g of bentonite powder was mixed with 100 mL of LAS solution with the concentration of LAS equivalent to 1.5 times the CEC of the raw bentonite. The mixture was then subjected to microwave heating (National NN-S327 WF) at a heating power of 700 W for 5 min. The resultant organo-bentonite was then washed several times with deionized water and dried in an oven at 105°C for 2 h. Finally, the organo-bentonite was crushed, sieved and kept in a desiccator until further use.

2.3   Characterizations of adsorbents

The XRD patterns of raw bentonite and organo-bentonite were obtained with a Bruker DS Advance powder diffractometer at 40 kV, 40 mA and a step size of 0.01° using CuKα radiation. The FTIR spectra of the adsorbents were recorded with a Shimadzu 8400S spectrometer in the wavenumber range of 500 to 4000 cm^{-1}, using a KBr disk procedure.

2.4   Adsorption experiments

Adsorption experiments were conducted in a static mode at three different temperatures (303.15 K, 313.15 K and 323.15 K). A stock solution of copper ions with an initial concentration of 400 mg/L was prepared by dissolving a fixed amount of $CuSO_4·5H_2O$ into 1 L deionized water. The adsorption equilibrium experiments were carried out by adding various masses of adsorbents (0.1–1.0 g) to a series of conical flasks containing 50 mL of metal solution. Subsequently, the flasks were placed in a water-bath shaker equipped with a temperature controller (Memmert SV-1422) and shaken at 200 r·min^{-1} for 1–2 h to reach equilibrium. The metal solution was then centrifuged at 2500 r·min^{-1} for 10 min to remove the solid particles. The residual concentration of Cu(II) ions in the metal solution was determined by flame atomic absorption spectrophotometer at λ_{max} = 324.6 nm.

For adsorption kinetics, the experiments were conducted as follows: 0.1 g of organo-bentonite was added to a series of conical flasks containing 50 mL of metal solution with initial concentrations of 400 mg/L. The flasks were then placed in a thermostated shaker and heated from room temperature to the desired temperature (303.15 K, 313.15 K or 323.15 K). The shaker was then set at 200 r·min^{-1} for a given period of time. At regular time intervals, 10 mL of metal solution was removed from the flasks, centrifuged and analyzed for its residual metal ion concentration. All experiments were carried out in triplicate with their averages used as the result. The effect of pH on the adsorption process was also studied in the pH range of 1–5. Higher pH values were not used since copper ions precipitate to form $Cu(OH)_2$ at higher pH (more basic condition). To adjust the pH, an appropriate amount of 0.1 mol·L^{-1} HCl solution was added.

The amount of Cu(II) ions adsorbed on a solid surface at equilibrium (q_e), in units of mmol/g, can be determined from the following mass balance equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}, \qquad (1)$$

where C_0 and C_e (mmol/L) are the concentrations of Cu(II) ions at initial and equilibrium conditions, respectively, V is the volume of solution (L) and m is the mass of raw bentonite or organo-bentonite used (g).

3   Results and discussion

3.1   XRD analysis

XRD analysis was performed to characterize the layered structure of the bentonite before and after modification with the LABORATORIES surfactant. The powder XRD patterns of raw bentonite and organo-bentonite (figures not shown here) had reflection peaks at about 2θ = 5.12° and

4.34°. These peaks correspond to the basal spacing, d(001) and represent the 2:1 layer thickness of smectites, with values of 1.724 and 2.012 nm for raw bentonite and organo-bentonite, respectively. The increased basal spacing in organo-bentonite indicates that the LAS molecules were partially intercalated into the interlayer spacing of bentonite thus lengthening its 2:1 interlamellar distance.

3.2   FTIR analysis

Table 1 presents the vibrational modes of various functional groups on the surface of raw bentonite and organo-bentonite from 500 to 4000 cm^{-1}.

The band at 3630 cm^{-1} indicates an O–H stretch in the silanol (Si–OH) or aluminol (Al–OH) groups. Asymmetric and symmetric C–H stretching bands for the ($-CH_2$)$_n$ in the LAS carbon chains on the organo-bentonite were seen at 2855–2925 cm^{-1}. The bending vibration at 1460 cm^{-1} is ascribed to the deformation of $-CH_2$, which is also observed in the organo-bentonite. The slight shift in the peak at 780 cm^{-1} (raw bentonite) to 795 cm^{-1} (organo-bentonite), which is the characteristic of the quartz Si–O stretch, denotes a change in structure in the interior of the raw bentonite during microwave heating.

3.3   Effect of pH

The effect of pH on the adsorption of Cu(II) ions onto organo-bentonite is shown in Fig. 1.

From Fig. 1, it can be seen that as the pH increases from 1 to 3, the amount of copper ions adsorbed increases from 0.03 to 0.07 mmol/g. In acidic solutions, the adsorption of copper ions is not favored due to the competitions with H$^+$. Increasing pH reduces the concentration of hydrogen ions in the metal solution and thus facilitates the mobility of the adsorbate molecules so they can penetrate into the solid surface. Increasing pH also leads to more negatively charged surface sites on the solid. These sites are associated with deprotonated silanol ($\equiv$Si–O$^-$) or aluminol ($\equiv$Al–O$^-$) species. This in turn, results in an electrostatic interaction between the Cu(II) ions and these species. Moreover, the presences of LABORATORIES anions at the interlayer of bentonite render a positive effect on the adsorption of copper ions promoting the electrostatic interactions between the negatively charged solid surface and the metal cations.

In the pH range of 3–6, the amount of metal ions adsorbed remains fairly constant. As previously mentioned, the pH study was limited to pH < 6.0 due to precipitation of copper ions as Cu(OH)$_2$ at higher pH. For this reason, pH 5 was selected as the optimum condition for subsequent studies on copper ion removal.

3.4   Adsorption isotherms

At equilibrium conditions, there is a defined relationship between the solute concentration in solution and that in the adsorbed state (i.e., the amount of solute adsorbed per unit mass of adsorbent). The correlation of adsorption equilibrium data with either a theoretical or an empirical equation is essential to describe adsorption behavior as well as to predict its extent. Different adsorption models, that were initially developed for gas phase adsorption and later extended to liquid phase adsorption, have been successfully applied to correlate adsorption equilibrium data for various systems. Since adsorption is a temperature-dependent process, it is logically assumed that adsorption models also exhibit temperature dependency. To this end, several adsorption models in their temperature-dependent forms were used to evaluate their applicability to the equilibrium data for the adsorption of copper ions onto organo-bentonite at various temperatures.

A Langmuir model was developed based on three assumptions: 1) adsorption is limited to monolayer coverage; 2) all solid surface sites are alike and 3) each surface site on the solid can only accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of the occupancy of its neighboring sites [15]. The Langmuir model is expressed mathematically as:

$$q_e = \frac{C_e q_{max} K_L}{1 + C_e K_L}, \qquad (2)$$

where q_e is the amount of Cu(II) ions adsorbed under equilibrium conditions (mmol/g); q_{max} is the maximum

Table 1   FTIR assignments of raw bentonite and organo-bentonite

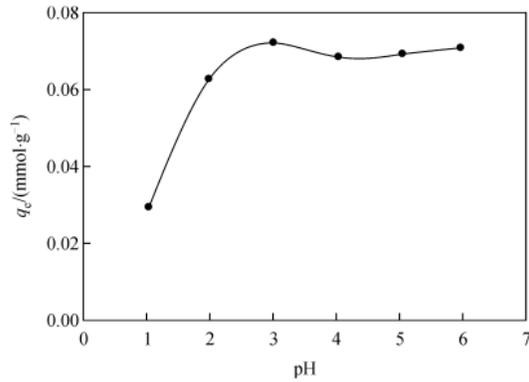| Assignments	Wavenumber /(cm^{-1})	
	Raw bentonite	Organo-bentonite
Al–OH or Si–OH stretch	3630	3624
Asymmetric C–H stretch of ($-CH_2$)$_n$	–	2925
(symmetric vibration)		2855
H–O–H bend	1640	1647
C–H in plane binding (for alkyl groups)	–	1465
O–H bend bounded with 2Al^{3+}	948	955
Si–O bend of quartz	780	795

Fig. 1 Effect of pH on the adsorption of Cu(II) ions onto organobentonite (Operation conditions: $C_0 = 400$ mg/L, adsorbent mass = 0.8 g, $t = 303.15$ K)

adsorption capacity of the adsorbent (mmol/g), corresponding to monolayer surface coverage; and K_L is the adsorption affinity constant or the Langmuir constant (L/mmol). The temperature-dependent forms of q_{max} and K_L are as follows [15,16]:

$$q_{max}(T) = q_0 \exp[\delta(T - T_0)], \qquad (3)$$

$$K_L(T) = K_{L_0} \exp\left(\frac{Q}{RT}\right). \qquad (4)$$

Here, q_0 is the adsorption capacity at the reference temperature (T_0), taken here as 298.15 K (mmol/g); δ is a parameter associated with the expansion coefficient of the adsorbate ions; K_{L_0} is the adsorption affinity at 298.15 K (L/mmol); Q is the heat of adsorption (J·mol^{-1}) and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}).

A Freundlich model was proposed on the assumption that the solid surface is heterogeneous in the sense that the adsorption energy is evenly distributed and the surface topography is patch-wise [15]. The Freundlich model can be expressed mathematically as follows:

$$q_e = K_F C_e^{\frac{1}{n}}. \qquad (5)$$

Here, K_F is the Freundlich parameter associated with the adsorption affinity [(mmol/g)·(mmol/L)$^{-n}$]; and n is a parameter that characterizes the system heterogeneity. The parameters K_F and n are temperature-dependent parameters with their mathematic equations as follows [15]:

$$\frac{1}{n} = \frac{RT}{A_0}, \qquad (6)$$

$$K_F(T) = K_{F_0} \exp\left(-\frac{\alpha RT}{A_0}\right), \qquad (7)$$

where K_{F_0} is the adsorption affinity of the solute at 298.15 K; A_0 is a characteristic of the adsorption potential (J/mol) and α is a constant.

The Sips or Langmuir-Freundlich equation is a three-parameter isotherm model that was proposed to circumvent the impossibility of a continual increase in the adsorbed amount as the adsorbate concentration increases, which is encountered in the Freundlich model [15]. The Sips equation has the form:

$$q_e = \frac{q_{max} (K_S C_e)^{\frac{1}{n}}}{1 + (C_e K_S)^{\frac{1}{n}}}. \qquad (8)$$

The temperature-dependent forms of K_S and n are expressed below:

$$K_S(T) = K_{S_0} \exp\left[\frac{Q}{RT}\left(\frac{T_0}{T} - 1\right)\right], \qquad (9)$$

$$n_S(T) = \frac{1}{\dfrac{1}{n_0} + \eta\left(1 - \dfrac{T_0}{T}\right)}, \qquad (10)$$

where K_S is the affinity coefficient (L/mmol); n_S is a parameter characterizing the system heterogeneity; K_{S_0} is the adsorption affinity at 298.15 K (L/mmol); n_0 is the value of n_S at 298.15 K and η is a constant. The temperature dependent form of q_{max} is given in Eq. (3).

The Toth equation is another three-parameter isotherm model that describes the adsorption behavior in heterogeneous systems. The Toth equation with its temperature dependency has the forms:

$$q_e = \frac{q_{max} \, b_T C_e}{[1 + (b_T C_e)^{n_T}]^{\frac{1}{n_T}}}, \qquad (11)$$

$$b_T(T) = b_0 \exp\left[\frac{Q}{RT}\left(\frac{T_0}{T} - 1\right)\right], \qquad (12)$$

$$n_T(T) = n_0 + \eta\left(1 - \frac{T_0}{T}\right). \qquad (13)$$

Here, b_T is the affinity coefficient (L/mmol); n_T is a characteristic parameter for the system heterogeneity; b_0 is the adsorption affinity at 298.15 K (L/mmol); n_0 is the value of n_T at 298.15 K and η is a constant. The values of b_T and n_T are specific for specific adsorbent-adsorbate pairs.

Figures 2–5 show the isotherm plots of the adsorption equilibrium data at various temperatures fitted to Langmuir, Freundlich, Sips and Toth models respectively. The model parameters were obtained by non-linear least squares fitting of the adsorption models to the experimental data and the results are summarized in Table 2. For this purpose, the sum of squares of the errors was employed as
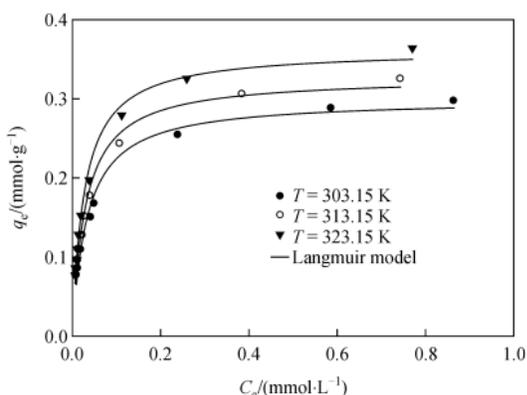
Fig. 2 Equilibrium plot of the adsorption of Cu(II) onto organo-bentonite at various temperatures–Langnuir model

the objective function to be minimized.

At a glance, Figs. 2–5 demonstrate that the Langmuir, Sips and Toth models can all represent the experimental data well (substantially better than the Freundlich model). Nevertheless, to confirm the validity of the models in representing the adsorption data, the theoretical justifications of each model's parameters need to be examined.

The q_0 values of organo-bentonite (0.29–0.34 mmol/g) obtained from the fitted Langmuir, Sips and Toth equations

are reasonable and comparable to the typical values obtained for the adsorption capacity of clay-based adsorbents [17–21]. The next important parameter used to evaluate the adequacy of the model is the heat of adsorption (Q). An inconsistent Q value (with respect to the experimental data) was observed for the Toth model. The fitted result for the Q parameter obtained by the Toth model leads to a positive Q value, indicating an exothermic process. In contrast, the experimental data in Fig. 5 shows that the adsorption capacity increases with temperature, denoting an endothermic process and indicating that thermal energy is required to make the process more favorable. Due to this inconsistency, the Toth model fails to give the best correlation with the experimental data.

The δ parameter relates closely to the expansion coefficient of the adsorbate ions. Its magnitude is normally on the order of $10^{-3}\,K^{-1}$ [16]. Accordingly, the δ values obtained from the nonlinear least squares fitting method with the Langmuir and Sips equations are consistent and thus it can be assumed that for this parameter, both equations provide adequate correlations with the experimental data.

The affinity parameter at 298.15 K (K_{L_0} and K_{S_0}) is a measure of the extent of interactions between the adsorbates and the solid surface. High values of affinity lead to an increase in the amount of solutes covering the solid surface. The fitted value of the affinity parameter obtained from the Langmuir model is unreasonably high,

Table 2 Fitted temperature dependent parameters for several adsorption equations for the adsorption of Cu(II) ions onto organo-bentonite

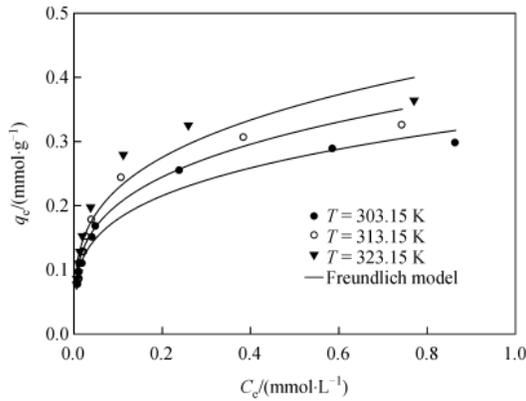| Adsorption equation	Parameter	Value
Langmuir	$q_0\ /(mmol \cdot g^{-1})$	0.285
	$K_{L_0}\ /(L \cdot mmol^{-1})$	1036.8
	$Q/(kJ \cdot mol^{-1})$	−8.94
	$\delta\ /(K^{-1})$	9.5×10^{-3}
Freundlich	$K_{F_0}\ /[(mmol/g) \cdot (mmol/L)^{-n}]$	0.0061
	α/A_0	−0.0016
	$A_0\ /(kJ \cdot mol^{-1})$	9.57
Sips	$q_0\ /(mmol \cdot g^{-1})$	0.326
	$K_{S_0}\ /(L \cdot mmol^{-1})$	17.59
	$Q\ /(kJ \cdot mol^{-1})$	−13.67
	$\delta\ /(K^{-1})$	7.8×10^{-3}
	n_0	1.458
	H	1.371
Toth	$q_0\ /(mmol \cdot g^{-1})$	0.3441
	$b_0\ /(L \cdot mmol^{-1})$	59.205
	$Q\ /(kJ \cdot mol^{-1})$	4.02
	$\delta\ /(K^{-1})$	6.7×10^{-3}
	n_0	0.5443
	H	1.8025

Fig. 3 Equilibrium plot of the adsorption of Cu(II) ions onto organo-bentonite at various temperatures–Freundlich model
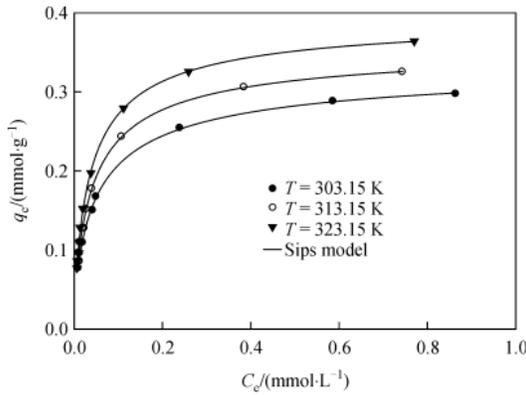

Fig. 4 Equilibrium plot of the adsorption of onto Cu(II) organo-bentonite at various temperatures–Sip smodel
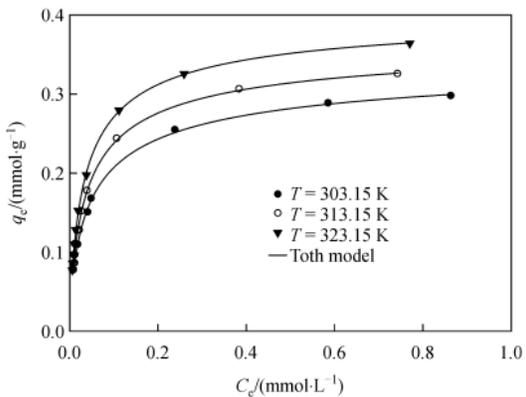

Fig. 5 Equilibrium plot of the adsorption of Cu(II) ions onto organo-bentonite at various temperatures–Toth model

especially considering the fact that the adsorption process occurs in the liquid phase. The Sips model, on the other hand, provides a more reasonable affinity value for the metal-ion-clay adsorbent system. Therefore, the only model which satisfies all theoretical justifications of the isotherm parameters is the Sips model.

3.5 Adsorption kinetics

In designing industrial adsorption systems, it is crucial to understand the kinetics of the adsorption process, especially the adsorption mechanism and the rate-controlling step. The latter information is generally required to optimize the operating conditions for full-scale batch metal removal processes. To this end, several kinetic models are available and the pseudo-first order and pseudo-second order are the most widely used for representing kinetic data.

The first order rate equation, also known as the pseudo-first order model was first proposed by Lagergren in the 19th century [22]. This model has the form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t), \tag{15}$$

where k_1 is the rate constant of the pseudo-first order model (min^{-1}). Integration of Eq. (15) with boundary conditions of $t = 0$, $q = 0$ and $t = t$, $q = q_t$ and rearrangement give:

$$q_t = q_e[1 - \exp(-k_1 t)]. \tag{16}$$

The pseudo-second order model is commonly used when the rate of the adsorption/desorption process controls the overall sorption kinetics. The mathematical expression of the model was first developed by Blanchard et al. [23]. The pseudo-second order model was derived on the basis of the adsorption capacity of the solid phase, and is expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2. \tag{17}$$

Here, k_2 is the rate constant for the pseudo-second order model (g·mmol^{-1}·min^{-1}). Integration of Eq. (17) with boundary conditions of $t = 0$, $q = 0$ and $t = t$, $q = q_t$ and rearrangement give:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t. \tag{18}$$

The kinetic parameters for the adsorption of Cu(II) ions onto organo-bentonite were calculated by nonlinear fitting of the models to the experimental data and the results are presented in Table 3.

Plots of the kinetic experimental data and the fitted pseudo-first and pseudo-second order models are shown in Figs. 6 and 7, respectively. The pseudo-second order model is a better fit than the pseudo-first order, which is indicated by the higher correlation coefficients (R^2).

Table 3 Fitted kinetic parameters for the adsorption of Cu(II) ions onto organo-bentonite

T /K	$q_{e,exp}$ /(mmol·g^{-1})	Pseudo-first order			Pseudo-second order		
		q_e/(mmol·g^{-1})	k_1/(min^{-1})	R^2	q_e/(mmol·g^{-1})	k_2/(g·mmol^{-1}·min^{-1})	R^2
303.15	0.2972	0.2903	0.1612	0.9486	0.3074	1.1271	0.9849
313.15	0.3243	0.3175	0.1795	0.9249	0.3335	1.2656	0.9928
323.15	0.3632	0.3550	0.1906	0.9166	0.3710	1.2868	0.9933
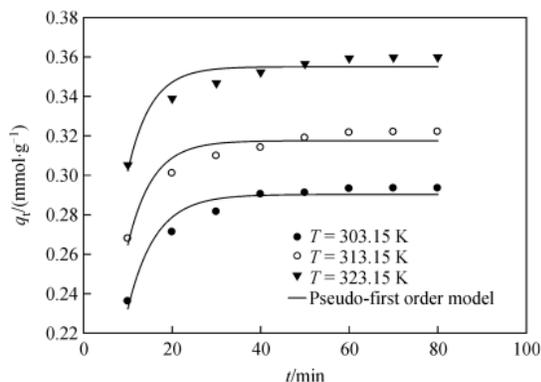
Fig. 6 Kinetic plot for the adsorption of Cu(II) ions onto organo-bentonite at various temperatures
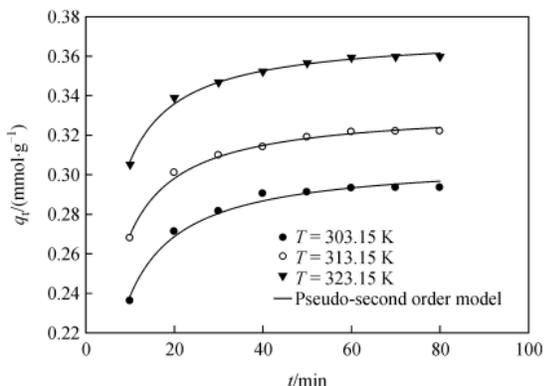
Fig. 7 Kinetic plot for the adsorption of Cu(II) ions onto organo-bentonite at various temperatures

In addition, the fitted values of q_e in the pseudo-second order model are consistent with the experimental q_e values. These results indicate that the adsorption process obeys a pseudo-second order model. In most cases, this model can predict very accurately the actual amount adsorbed at equilibrium due to its small sensitivity to random experimental error.

Generally, the value of k_2 strongly depends on the operating conditions, to the extent that this parameter can be regarded as a time-scaling factor due to its strong dependency on the initial solute concentration [24]. Moreover, temperature also plays an important role in the adsorption kinetics since a change in temperature results in a change in equilibrium conditions. This is evidenced by the increase in q_e from 0.3074 to 0.3710 mmol/g when the temperature is increased from 303.15 K to 323.15 K. A higher q_e value also translates to a higher value of k_2, resulting in a faster uptake of metal ions and a shorter time to reach an equilibrium state. Heating, therefore, promotes the adsorption process.

3.6 Thermodynamic studies

Thermodynamic parameters, i.e., changes in enthalpy (ΔH^0), entropy (ΔS^0) and Gibb's free energy (ΔG^0) are also important to completely evaluate the Cu-adsorption process. The calculation of the above thermodynamic parameters was conducted using the van't Hoff equations below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \qquad (19)$$

$$\Delta G^0 = -RT\ln K_D. \qquad (20)$$

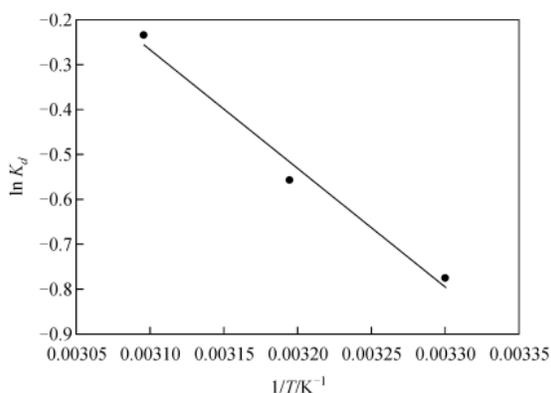Equations (19) and (20) can also be written in a linear form with respect to K_D and $1/T$ as follows:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \qquad (21)$$

where K_D is the thermodynamic distribution coefficient representing the equilibrium concentration of the solute on the solid surface (mmol/g) and the equilibrium concentration in the metal solution (mmol/g); ΔS^0 and ΔH^0 are the standard entropy (kJ·mol^{-1}·K^{-1}) and the standard enthalpy changes (kJ·mol^{-1}), respectively; ΔG^0 is the standard Gibb's free energy change (kJ·mol^{-1}) and R is the universal gas constant (8.314 × 10^{-3} kJ·mol^{-1}·K^{-1}). The values of ΔH^0 and ΔS^0 were obtained from the slope and intercept of a linear plot of $\ln K_D$ vs. $1/T$ as shown in Fig. 8. The thermodynamic parameters of the adsorption process are summarized in Table 4. The positive ΔH^0 value indicates the adsorption process is endothermic, which is consistent with the previous equilibrium and kinetic studies. The endothermic nature of the process is due to the strong interactions between the solid and the Cu(II)

Table 4 Thermodynamic parameters for the adsorption of Cu(II) ions onto organo-bentonite

T /K	ΔG^0/(J·mol^{-1})	ΔH^0 /(kJ·mol^{-1})	ΔS^0 /(J·mol^{-1}·K^{-1})	R^2
303.15	2005.54			
313.15	1346.82	21.96	65.87	0.9833
323.15	688.1			

Fig. 8 van't Hoff plot for adsorption of Cu(II) ions onto organo-bentonite

ions, where energy is required for the initial stripping of the metal ions from their hydration shells [2].

Furthermorpe, one of the possible adsorption mechanisms between Cu(II) ions and organo-bentonite involves the exchange of metal ions with H$^+$ ions. This requires an input of energy for the cleavage of the hydroxyl group hydrogen bonds prior to the cation exchange.

The positive ΔS^0 value reveals the increased degree of randomness at the solid-solution interface during the adsorption process. This is probably due to the structural changes in the solid caused by the intercalation of metal ions, the release of hydrated water during the metal ions' transition and the distribution of rotational and translational energies among the solute molecules in the adsorbed state [25]. The positive ΔG^0 values indicate the process is non-spontaneous and needs energy from an external source, e.g., thermal energy from heating, to occur. Moreover, an increase in temperature decreases the values of ΔG^0, possibly due to the dehydration of water molecules from the hydration shells of the copper ions [26].

Another important thermodynamic parameter is the activation energy for the adsorption process. This parameter can be used to identify whether the adsorption process is physical or chemical. Physisorption has activation energies between 5 and 40 kJ/mol whereas higher values (40–800 kJ/mol) suggest chemisorption. The activation energy can be determined from the pseudo-second order rate constant, k_2, by the Arrhenius equation below:

$$\ln k_2 = \ln A - \frac{E_a}{RT}. \qquad (22)$$

Here, A is the temperature-independent Arrhenius constant and E_a is the activation energy (kJ·mol^{-1}). The activation energy can be determined from the slope of an Arrhenius plot of lnk_2 vs. 1/T. This plot (not shown here) gave E_a = + 40.2 kJ/mol, indicating that adsorption of Cu(II) ions onto organo-bentonite occurs via chemisorption.

4   Conclusions

Organo-bentonite was prepared via modification of bentonite using linear alkyl benzene sulfonate surfactant via microwave heating. Adsorption experiments were carried out in a static mode at various temperatures (303.15 K, 313.15 K and 323.15 K) and at pH 5. For correlations of the adsorption equilibrium data, the temperature dependent forms of the Langmuir, Freundlich, Sips and Toth equations were employed. Based on the theoretical justifications of each model parameter, the Sips equation demonstrates the best representation of the adsorption equilibrium data. For the kinetic data correlation, the pseudo-second order model was superior to the pseudo-first order model. Thermodynamically, the adsorption of Cu(II) ions onto organo-bentonite occurs via chemisorption and the process is endothermic, irreversible and non-spontaneous.

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