



Heavy metal removal from water by sorption using surfactant-modified montmorillonite

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Abstract

Removal of Cu^{2+} and Zn^{2+} from aqueous solutions by sorption on the montmorillonite modified with sodium dodecylsulfate (SDS) was investigated. Experiments were carried out as a function of solution pH, solute concentration, and temperature (25–55 °C). The Dubinin–Kaganer–Radushkevick model was adopted to describe the single-solute sorption isotherms. Also, the binary-solute sorption equilibria could be reasonably predicted by the competitive Langmuir model, in which the Langmuir parameters were directly taken from those obtained in single-solute systems. The thermodynamic parameters (ΔH° and ΔS°) for Cu^{2+} and Zn^{2+} sorption on the modified clay were also determined from the temperature dependence. The kinetics of metal ions sorption was examined and the pseudo-first-order rate constant was finally evaluated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sodium dodecylsulfate; Montmorillonite; Cu^{2+} ; Zn^{2+} ; Sorption isotherm; Kinetics

1. Introduction

Many toxic heavy metals have been discharged to the environment as industrial wastes, causing serious soil and water pollution. Various physicochemical and biological methods were studied for metal removal. Use of clays as sorbents to remove contaminants has been increasingly paid attention because they are cheaper than other materials such as activated carbon and zeolite. Clays are widely applied in many fields of technology and science, for example, the removal of liquid impurities and purification of gases [1–3]. Such a wide usefulness of clays is a result of their high specific surface area, high chemical and mechanical stability, and a variety of surface and structural properties. The chemical nature and pore structure generally determine the sorption ability of clay. For gas-phase sorption, the pore structure,

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i.e. the nature and volume of pores, is a predominant factor. In the case of liquid-phase sorption, the chemical properties of surface groups influence the extent of sorption.

The Na^+ -type of montmorillonite, which is a 2:1 layered silicate that swells when it contacts by water. The inner layer is composed of an octahedral sheet of the general form $\text{M}_{2-3}(\text{OH})_6$ (where M is typically Al^{3+}), which is situated between two SiO_4 tetrahedral sheets [4]. The replacement of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative charge on the clay surfaces. The charge imbalance is offset by exchangeable cations such as H^+ , Na^+ , or Ca^{2+} on the layer surfaces. In aqueous solutions, water is intercalated into the interlamellar space of montmorillonite, leading to an expansion of the minerals. Clays, although with the negative surface charge, have little or weakly affinity for heavy metal ions such as Co^{2+} , Zn^{2+} , and Cu^{2+} .

Managed by acid or ion exchange with surfactants have been widely used to alter the surface properties of the swelling clays and other nature materials in order to improve the sorption ability [4–8]. Most of the previous studies focused on using cationic surfactants to sorb organic matter or metallic anions; e.g. the sorption of phenol and alkylphenols on HDTMAB (hexadecyltrimethylammonium bromide)-modified montmorillonite [6] and anion–cation organobentonite [4]. In addition, the sorption of Cr(VI) anions on modified montmorillonite [6], zeolite [7], and natural clinoptilolite [9,10] were presented. In fact, the modification mechanism depends on the nature of clays (degree of swelling, layer structure) and surfactants (molecular size). Haggerty and Bowman [7] reported that amine surfactants are too large to enter the internal position of zeolite and sorption of the amines only occurs on the zeolite's external exchange sites.

Relatively few studies have been made for sorption of heavy metal cations on clays modified with anionic surfactants such as sodium dodecylsulfate (SDS). The sorption of metal ions by naturally available clays was not paid much attention, perhaps due to the weakly binding strength between them. Since bentonite clays are swelling in nature, large anionic species such as SDS can easily enter and become fixed strongly in the interlayer region of, e.g. montmorillonite [11]. In order to sorb metal cations and form complexes, the clay surface must possess negatively charged sites or there should be a replacement of weakly held counter-ions in the solution. Sorption of metal cations on anionic surfactant modified clays has been due to the formation of a surface-cation complex [12].

The aim of this work was to provide fundamental equilibrium and kinetic information in the sorption of Cu^{2+} and Zn^{2+} from single and binary solute solutions on SDS-modified montmorillonite. Many parameters including sorption capacity, sorption energy, enthalpy change, and entropy change were determined. These parameters would be very useful in the understanding of sorption removal of heavy metals by modified clays from an aqueous environment.

2. Experimental

2.1. Clay and reagents

Montmorillonite KSF was purchased from Fluka, which had an idealized formula of $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The BET specific surface area was measured to be $8.9 \text{ m}^2/\text{g}$ from N_2

sorption isotherms with a sorptiometer (Quantachrome NOVA 2000). Its cation exchange capacity (CEC) was 37.2 mmol/100 g. Sodium dodecylsulfate (SDS) was provided from Mallinckrodt Co. Metal sulfates (CuSO_4 , CoSO_4 , ZnSO_4) and other inorganic chemicals were supplied by Merck as analytical grade reagents. The solution pH was adjusted by adding a small amount of 0.1 M HCl or NaOH.

2.2. Preparation and characterization of the modified clay

The modification of the clay was carried out as follows. A known amount of SDS ranging from 10 to 30 mM was dissolved separately in 1 l of deionized water (Milli-Q, Millipore). Twenty grams of the clay and acetone (5 ml) were added to the SDS solution. Acetone was used to make the clay suspension less sticky and easier to handle. The contents were mixed thoroughly in a shaker for 2 h. Preliminary experiments had shown that the final amount of SDS sorbed was kept unchanged after the sample was shaken for more than 1 h. The mixture was centrifuged and the solid was washed about five times with deionized water to remove superficially SDS sorbed on the surface. The amount of SDS sorbed was determined by a CHN elemental analyzer (Carlo Erba Model EA1108). Such a quantity was found to increase with increasing the concentration of added surfactant. Zeta potentials of the clay suspensions were measured using Malvern Zetasizer system (Model 3000).

To examine whether the SDS molecules were intercalated, the treated samples were washed to remove any surfactant on the surface and subjected to X-ray diffraction analysis. The $d(001)$ reflections by powder XRD method for the untreated clay as well as the treated clay before and after metal sorption were recorded with a low angle XRD facility (JOEL, JSMT S330). Since the $d(001)$ values showed a clear swelling of the sheets as a result of SDS treatment, modification of surfactant must have taken place inside the interlamellar region of the montmorillonite. Before each measurement, the samples were degassed at 110 °C for 10 h.

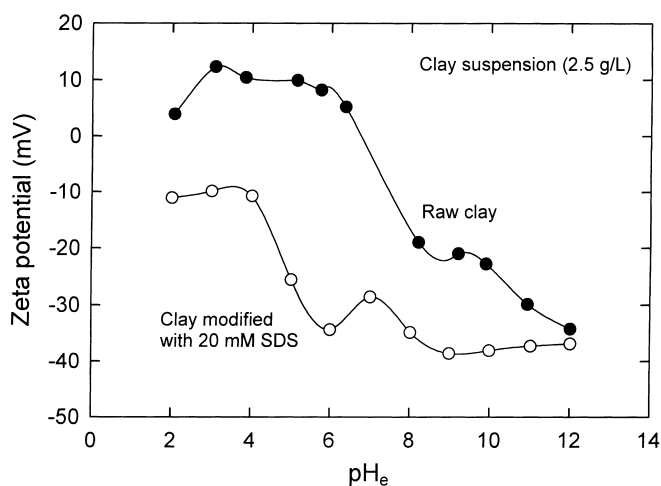


Fig. 1. Zeta potentials of the clay suspensions (2.5 g/l).

2.3. Sorption of metal ions

For the sorption of metal ions, 0.25 g of air-dried SDS-modified clay was used in a batch vessel at various fixed temperatures. The modified clay was contacted with different concentrations of Cu^{2+} and/or Zn^{2+} ranging from 4.5 to 45 mmol. The mixture (100 ml) was allowed to shake for 3 h and was then centrifuged at 2500 rpm for 10–60 min. The concentration of metals in the centrifuges was determined by a Varian atomic absorption spectrophotometer (Model 220FS), and the pH was measured with a Horiba F-23 pH meter. The amount of metals sorbed on the clay was calculated from a mass balance relationship. Each experiment was performed twice at least under identical conditions. Reproducibility of the measurements was mostly within 4%. In some runs, samples were taken at preset time intervals to investigate the kinetics of sorption.

3. Results and discussion

3.1. Properties of the modified montmorillonite

The $d(100)$ values of raw montmorillonite, the SDS-modified clays before and after metal sorption are different (not shown). The XRD patterns indicate that they have a lamellar structure with an average basal spacing of 1.41, 2.11, and 2.11 nm, respectively. Krishna et al. [5] also reported that the $d(100)$ values of raw montmorillonite, the clays modified with HDTMAB before and after sorption of Cr(VI) anions are 1.41, 3.2, and 3.94 nm, respectively. Gallery expansion occurs due to the grafting of SDS to silanol groups within the interlayer where the silica framework is in contact with the clay layers. The BET surface area of SDS-modified montmorillonite ($80.3 \text{ m}^2/\text{g}$) is much larger than that of raw clay ($8.9 \text{ m}^2/\text{g}$). However, the result is opposite to some those reported earlier [13], where the surface areas of clays become small after surfactant modification. Such a difference is likely due to the comparatively larger particle size of the raw clay used in this work (i.e. the low specific surface area).

Fig. 1 shows the zeta potentials of the raw and SDS-modified clay suspensions at different pH values. The positively charged surface of the raw clay at pH 2–7 explains ineffective sorption of heavy metal cations. It is found that the clay modified with 20 mM SDS lowers the zeta potential up to 40 mV, resulting an enhancement of sorption ability of metal cations.

3.2. Equilibrium sorption of single metal ions

As shown in Fig. 2, the amount of metal sorption on the modified-clay decreases with increasing the weight of the clay. However, this tendency is not apparent for the raw clay and the clay modified with low SDS contents (<10 mM). This is likely because the water swelling is easier in the case of few amounts of clay. After grafting of SDS to the clay interlayer, the negative charge at clay surface increases apparently, and will increase with increasing pH values.

The raw montmorillonite has two kinds of acidic groups (XNa and SOH) [3] and exists as a negatively charged particle in the aqueous solutions; however, it weakly binds with metal

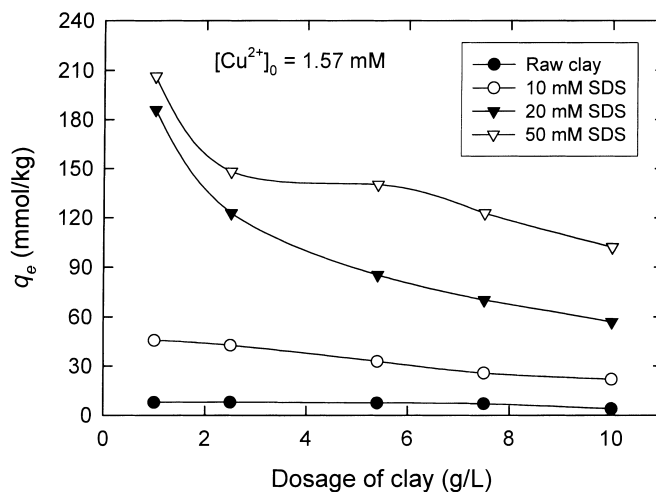


Fig. 2. Effect of dosage of the modified clay on the amount of Cu^{2+} sorption.

cations. After SDS modification, most clay surface is intercalated with SDS (RSO_3Na). The exchange reactions in solutions during sorption are shown below:

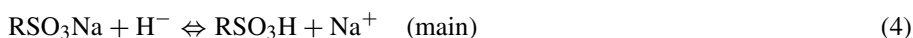
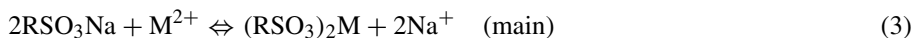
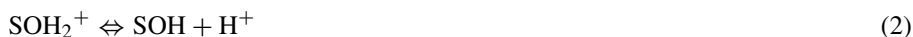


Fig. 3 shows the effect of equilibrium pH on the amount of sorption of single metal ions by modified clay. Apparently, the amount of sorption q_e increases with increasing pH for both metal ions. The sorption of these ions is primarily affected by the surface charge on the sorbent, which in turn is influenced by solution pH [14]. The low q_e at low pH may be explained by the competitive sorption between proton and metal ions. As the solution pH increases, the number of negatively charged sites increases (Fig. 1), which favors the sorption of metal cations. The amount of Cu^{2+} sorbed is larger than that of Zn^{2+} , as have been also observed previously [15]. The difference in the amount of sorption between two metals is dependent of their equilibrium constants shown in Eq. (3).

3.3. The DKR and Langmuir equations

The Dubinin–Kaganer–Radushkevick (DKR) and the Langmuir equations have been used to describe the sorption of metal ions on surfactant-modified clays [5,16]. The DKR equation has the following form

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

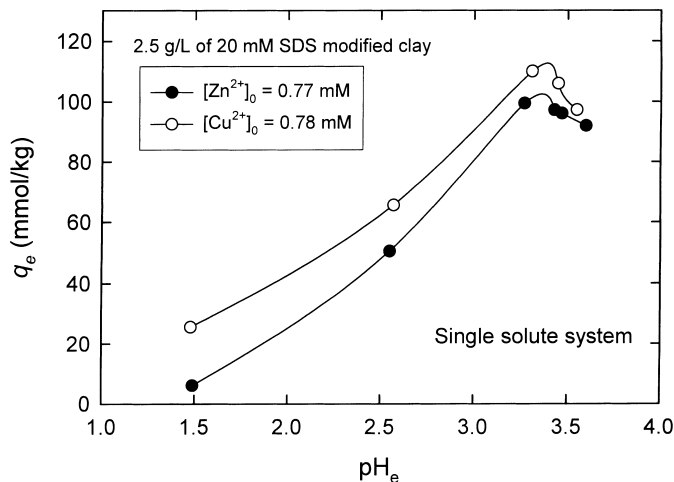


Fig. 3. Effect of equilibrium pH on sorption of Zn^{2+} and Cu^{2+} in single solute system using the montmorillonite modified with 20 mM SDS.

where q_e is the amount of sorption of metal ions in mmol/kg, q_m the DKR monolayer capacity, β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows

$$\varepsilon = RT \ln \left(\frac{1}{C_e} \right) \quad (6)$$

where T is the temperature in K and C_e is the equilibrium solution concentration of solute in mM. The slope of the plot of $\ln q_e$ versus ε gives β (mol^2/J^2) and of the intercept yields the sorption capacity, q_m (mmol/kg). The DKR parameters are listed in Table 1. According to following relationship [5,16], we could further obtain the sorption energy (E)

$$E = -\frac{1}{\sqrt{-2\beta}} \quad (7)$$

As shown in Table 1, the E values are -12.6 kJ/mol for Zn^{2+} sorption and -13.8 kJ/mol for Cu^{2+} sorption on the modified clay. They are the orders of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol [17,18]. The sorption capacity q_m in the DKR equation is found to be 31.9 mmol/kg for Zn^{2+} and 83.0 mmol/kg for Cu^{2+} .

Table 1
Parameters obtained in the DKR equation

DKR parameters	Cu^{2+} sorption	Zn^{2+} sorption
q_m (mmol/kg)	83.0	31.9
β (mol^2/J^2)	-9.9×10^{-9}	-1.3×10^{-8}
Sorption energy (E , kJ/mol)	-13.8	-12.6
Correlation coefficient, r^2	0.962	0.978

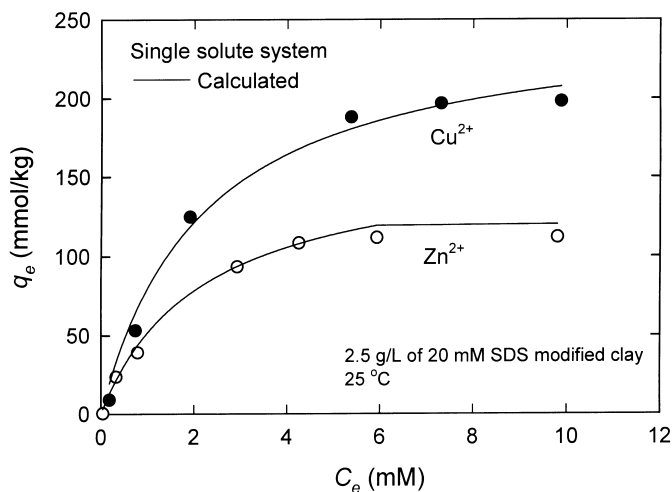


Fig. 4. The calculated Langmuir and measured isotherms for sorption of Zn^{2+} and Cu^{2+} in single solute system using the montmorillonite modified with 20 mM SDS.

The single-solute sorption isotherms for Zn^{2+} and Cu^{2+} by modified montmorillonite at 25 °C and pH 3 are shown in Fig. 4. Data correlating with the Langmuir equation are used to interpret the results, which is given by

$$q_e = \frac{K_L S_m C_e}{1 + K_L C_e} \quad (8)$$

where S_m is the amount of sorption corresponding to complete surface coverage (mmol/kg) and K_L is the Langmuir constant (l/mmol). Eq. (8) can be rearranged to a linear form

$$\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (9)$$

The isotherms are well described by the Langmuir equation (Fig. 4), in which the standard deviation (S.D.) as defined in Eq. (12) is 2.3%. The values of S_m are 202.9 mmol/kg for Zn^{2+} and 254.1 mmol/kg for Cu^{2+} using modified montmorillonite. They are much larger than those obtained by the DKR equation (q_m), so the DKR equation is mainly applicable in the low C_e region [5,16]; e.g. 0.156–1.56 mM for metal sorption in this work. Krishna et al. [5] also found the sorption capacity q_m at the DKR region to be 340 mmol/kg for sorption of Cr(VI) anions on HDTMAB-modified montmorillonite, but obtained a corresponding S_m value of 795 mmol/kg from the Langmuir equation.

One of the essential characteristics of the Langmuir equation could be expressed by dimensionless constant called equilibrium parameter, R_L [8]

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (10)$$

where C_0 is the highest initial solute concentration (mM). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or

Table 2
The Langmuir constants obtained for sorption of metal ions

Metals	Langmuir constants			R_L
	r^2	S_m (mmol/kg)	K_L (l/mmol)	
Cu^{2+}	0.975	254.1	0.46	0.52
Zn^{2+}	0.986	202.9	0.47	0.52

unfavorable ($R_L > 1$). It is shown that the sorption of both metal ions on modified clay is favorable (Table 2).

3.4. Equilibrium sorption of binary metal ions

The competitive Langmuir model is an extended form of the Langmuir model which allows to predict the amount of sorption of solute i per unit weight of sorbent, $q_{e,i}$, in the presence of other solutes [6,18]

$$q_{e,i} = \frac{S_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{i=1}^N K_{L,i} C_{e,i}} \quad (11)$$

where $C_{e,i}$ is the equilibrium solution concentration of solute i in the mixture, and $K_{L,i}$ and $S_{m,i}$ are the parameters determined by fitting the Langmuir model to the single solute i alone. The batch sorption experiments of the two ions, Zn^{2+} and Cu^{2+} , on SDS-modified clay were carried out at 25 °C. The sorption data are shown in Fig. 5, together with those calculated by the competitive Langmuir model. A close agreement is observed under the

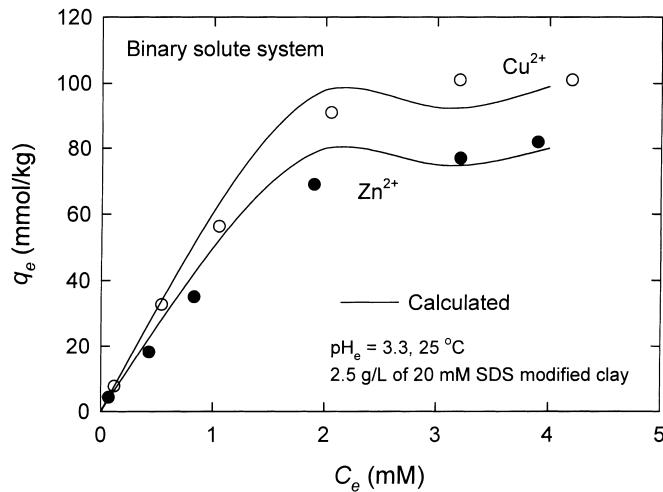


Fig. 5. The calculated and measured isotherms for sorption of Zn^{2+} and Cu^{2+} in binary solute system using the montmorillonite modified with 20 mM SDS.

ranges studied, indicating the validity of this model. The standard deviation (S.D.) defined in Eq. (12) is below 9%.

$$\text{S.D.} = 100 \sqrt{\frac{\sum [(q_{e,i}^{\text{cal}} - q_{e,i}^{\text{exp}}) / q_{e,i}^{\text{exp}}]^2}{n - 1}} \quad (12)$$

where n is the number of data points, and the superscripts “cal” and “exp” refer to the calculated and measured values, respectively.

3.5. Thermodynamic parameters

The amounts of sorption of single metal ions by SDS-modified clay are measured in a temperature range 25–55 °C. The equilibrium partition constant K_d is calculated as follows

$$K_d = \frac{q_e}{C_e} \quad (13)$$

The following relationships have been used to evaluate the thermodynamic parameters ΔG° , ΔH° , and ΔS° [4,16]

$$\Delta G^\circ = -RT \ln K_d \quad (14)$$

$$\log K_d = \left(\frac{\Delta H^\circ}{2.303R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad (15)$$

The change in free energy (ΔG°) is calculated to be -9.17 kJ/mol for Zn^{2+} and -9.66 kJ/mol for Cu^{2+} at 25 °C from Eq. (14). The negative values of ΔG° mean that the sorption of metal ions on modified clay is spontaneous, perhaps because the surfactant molecules have more affinity toward the metal ions. As clearly shown in Eq. (15), a plot of $\log K_d$ versus $1/T$ would give ΔH° and ΔS° (Fig. 6) (S.D. = 4.7%). The values of ΔH° and ΔS° (25 °C) are 7.39 kJ/mol and 6.39 J/mol K for Zn^{2+} as well as 7.05 kJ/mol and 9.09 J/(mol K) for Cu^{2+} . A slightly positive entropy change for sorption of metal ions on the modified clay is due to the fixation of ions on the exchange sites of the randomly distributed surfactant species.

3.6. Sorption kinetics of single metal ions

The kinetics of sorption of metal ions by modified clay was studied for its possible importance in treatment of metal-bearing industrial effluents. The pseudo-first-order rate constants for Zn^{2+} and Cu^{2+} are determined using the following equation [5,16,19]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (16)$$

where q_t refers to the amount of sorption at any time t . The plot of $\ln(q_e - q_t)$ versus t shows a straight line, indicating the applicability of the first-order kinetics (Fig. 7) (S.D. = 1.2%). The sorption is rapid during the first 10 min and the equilibrium is then attained within 30 min. The pseudo-first-order rate constants k_1 for Zn^{2+} and Cu^{2+} sorption on

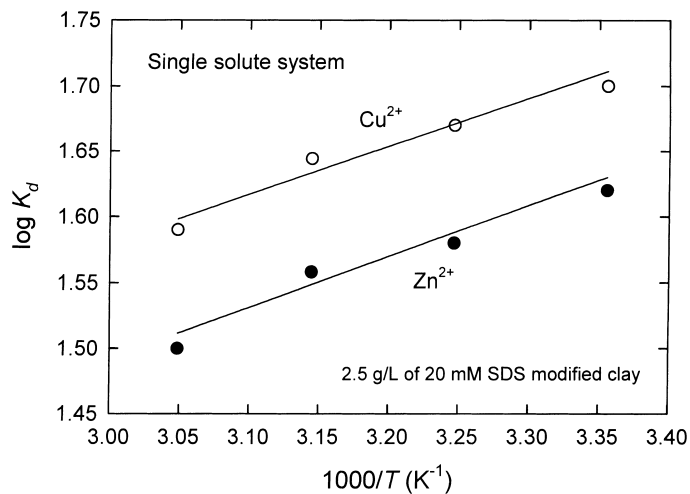


Fig. 6. Determination of thermodynamic parameters for sorption of Zn^{2+} and Cu^{2+} in single solute system using the montmorillonite modified with 20 mM SDS.

modified montmorillonite are calculated to be 6.64×10^{-4} and $3.14 \times 10^{-3} \text{ min}^{-1}$, respectively at 25°C . The sorption of Zn^{2+} and Cu^{2+} is faster than that of Cr(VI) anions on HDTMAB-modified clay [15]. In a word, the acceptably high capacity and fast kinetics for metal sorption on SDS-modified clays indicates their promising potential for treatment of industrial effluents with trace amounts of heavy metals.

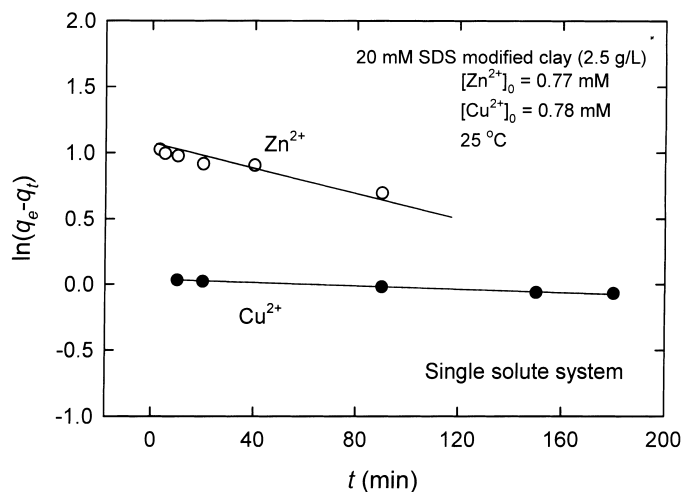


Fig. 7. Determination of rate constant for sorption of Zn^{2+} and Cu^{2+} in single solute system using the montmorillonite modified with 20 mM SDS.

4. Conclusions

Sorption removal of Cu^{2+} and Zn^{2+} from single and binary solutions using naturally available montmorillonite was studied. The clay was modified by anionic surfactant SDS, which penetrated into interlamellar region of the clay by the expansion of clay sheets in the *c*-axis. The following equilibrium and kinetic results were obtained.

Comparing to the raw clay, the SDS-modified clay suspension showed a much more negative zeta potential under the pH range examined, indicating a higher affinity for metal cations. In addition, the amount of sorption of both metal ions on modified clay increased with increasing solution pH.

The DKR and Langmuir equations were used to describe the sorption isotherms of single solute systems. The sorption energy E determined in the DKR equation (-12.6 kJ/mol for Zn^{2+} , -13.8 kJ/mol for Cu^{2+}) revealed the nature of ion exchange mechanism in both systems. The sorption isotherms of binary solute systems could be fitted by the competitive Langmuir model, where the Langmuir parameters were directly adopted from those obtained in single solute systems.

The thermodynamic parameters ΔH^0 and ΔS^0 for Zn^{2+} sorption on SDS-modified clay were 7.39 kJ/mol and 6.39 J/mol K), as well as 7.05 kJ/mol and 9.09 J/mol K) for Cu^{2+} sorption, respectively. A slightly positive ΔS^0 was due to the fixation of metal ions on the exchange sites of the randomly distributed surfactant species.

The sorption of metal ions on modified clay was rapid during the first 10 min and the equilibrium was attained within 2 h. The pseudo-first-order rate constants for Zn^{2+} and Cu^{2+} sorption were found to be 6.64×10^{-4} and $3.14 \times 10^{-3} \text{ min}^{-1}$, respectively at 25°C .

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