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Adsorption of Cu(II) onto three types of engineering materials in the presence of S,S-EDDS chelate: equilibrium, kinetics, and thermodynamics

Jianzhong Zhu, Ying Ding, Shenglu Chen, Yang Cao*

Key Laboratory of Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China, Tel. +86 13739186298; email: zhuhhai2010@hhu.edu.cn (J. Zhu), Tel. +86 18751958626; email: 987203352@qq.com (Y. Ding), Tel. +86 15295512755; email: luneng66@126.com (S. Chen), Tel. +86 15335195841; email: caoyanghehai@126.com (Y. Cao)

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ABSTRACT

The adsorption of Cu(II) ions in the presence of the S,S-ethylenediaminedisuccinic acid (S,S-EDDS) chelating agent was investigated to determine the adsorption characteristics of the 719 strongly basic anion exchange resin (719 resin), γ-Al_2O_3, and activated carbon (AC). The influence of adsorption pH (3–7), time (10–600 min), initial concentration (25–175 mg/L), and temperature (298–318 K) was determined. A mechanism for the adsorption process was proposed. The adsorption data were fitted to the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models. Batch experiments revealed that the maximum adsorption capacities are 17.46, 5.79, and 5.46 mg/g for the 719 strongly basic anion exchange resin, γ-Al_2O_3, and AC, respectively, at pH 6. The results also indicate that the Langmuir and Temkin adsorption models described the adsorption of Cu(II) ions onto the 719 strongly basic anion exchange resin, γ-Al_2O_3, and AC better than the Freundlich model. The obtained results show that a pseudo-second-order model describes the adsorption kinetics better than the other models for the three types of engineering materials. Thermodynamic constants for adsorption such as ΔH° and ΔS° were also calculated and we found that Cu(II) complex adsorption onto three types of engineering materials is an endothermic and spontaneous process.

Keywords: Adsorption; Copper (II); S,S-EDDS; Kinetics

1. Introduction

The removal of heavy metal ions is one of the most important current environmental problems. An increasing amount of toxic heavy metal ions [1,2] are being discharged into the environment and these include metals such as mercury, lead, copper, zinc, cadmium, and arsenic. Among these, copper is widespread in industrial wastewater [3] from industries such as mining, smelting of metalliferous ores, electroplating, leather processing, electrical appliance manufacturing, and metal surface treatment. Copper ions are environmentally unfriendly and toxic to humans when released inappropriately. Excess copper can disrupt human metabolism, cause cirrhosis and liver ascites, and even cause cancer [4–7]. Methods for the removal of copper ions from aqueous solutions mainly involve chemical precipitation, chemical and electro coagulation, filtration, ion exchange, electrochemical

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*Corresponding author.

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treatment, and adsorption. Adsorption is one of the most popular methods for heavy metal ion separation, removal, and recovery from different types of wastewater [8]. Activated carbon (AC), ion exchange resins, and mineral oxides are widely used in the removal of heavy metals from water and wastewater because they are economic, are easily prepared, and are of high efficiency. However, the presence of chelating agents in the aquatic environment affects the performance of adsorbents toward the removal of heavy metals [9]. Because of their strong complexes with heavy metal ions (such as Hg, Pb, Cu, Zn, and Cd), chelating agents have played an irreplaceable role in environmental remediation [10,11], and they have been applied to wastewater treatment and soil remediation. Because of the widespread use of chelating agents in detergents, industrial water treatment, galvanic processes, textiles, pigments, and oil production [12], it is important to study the effectiveness of heavy metal removal from water and wastewater in the presence of chelating agents.

The treatment of water and wastewater containing metal ions depends greatly on the particular chelating agent. Many types of chelating agents such as EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), HEDTA ((hydroxyethyl)ethylenediaminetriacetic acid) and S,S-EDDS (S, S-ethylenediaminedisuccinic acid) are commonly used. Among these chelators, EDTA, DTPA, and HEDTA have proven to be practically non-biodegradable in standard tests [13]. However, S,S-EDDS has attracted widespread attention because of its nature and its biodegradation properties in recent years [14]. As a biodegradable structural isomer of EDTA, S,S-EDDS has high complex stability and extraction efficiency toward many heavy metals. S,S-EDDS has been proposed to be an emerging substitute for EDTA.

Currently, S,S-EDDS is used as a bioremediation agent in heavy metal contaminated soils and this is commonly used all over the world. However, few reports have focused on the treatment of heavy metal wastewater using sorbents in presence of S,S-EDDS. The objective of this study was to investigate the removal of Cu(II) ions from an aqueous solution in the presence of S,S-EDDS using the 719 strongly basic anion exchange resin, γ-Al_2O_3, and AC. We chose these engineering materials because of their low cost, high efficiency, and commercial availability for environmental modification.

Complexation in the M(II):S,S-EDDS = 1:1 system can be expressed as Eq. (1) [15]:

$$M^{2+} + H_n\text{edds}^{n-4} \leftrightharpoons [MH_n edds]^{n-2} \tag{1}$$

For Cu(II) ions, the formation of the following complexes was assumed: $[Cu(H_2edds)]$, $[Cu(Hedds)]^-$, $[Cu(edds)]^{2-}$, $[Cu(OH)(edds)]^{3-}$, $[Cu(H_2edds)_2]^{2-}$, $[Cu(H_2eeds)(Hedds)]^{3-}$, $[Cu(Hedds)_2]^{4-}$, $[Cu(Hedds)edds]^{5-}$, and $[Cu_2edds]$ [16]. We found that in the Cu (II):S,S-EDDS = 1:1 system, the copper ions were 60% complexed with EDDS at pH 6 and the complexes were of the $[Cu(edds)]^{2-}$ type [17].

The 719 strongly basic anion exchange resin is in the Cl^- form and it can exchange with anions such as $[Cu(Hedds)]^-$, $[Cu(edds)]^{2-}$, and $[Cu(OH)(edds)]^{3-}$. The formation of anionic complexes between Cu(II) ions and S,S-EDDS allows for the removal of copper ions using anion exchangers. γ-Al_2O_3 and AC possess high specific surface areas that can adsorb anions and cations. Ion exchange, hydrogen bond interactions, and electrostatic adsorption are also possible mechanisms for Cu(II)–S,S-EDDS adsorption onto the used materials.

In this study, the influence of different parameters such as the Cu(II) ion concentration, pH, contact time, and temperature was determined to quantify the effectiveness of the S,S-EDDS chelate toward Cu(II) ion adsorption. The results are useful for applications that may be limited by the amount of absorbed heavy metals from water and wastewater.

2. Experimental

2.1. Materials and chemicals

All reagents were of analytical reagent grade unless otherwise specified. Deionized water was used for solution preparation. Stock solutions (6,000 mg/L) of Cu(II) were prepared using copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, Nanjing Chemical Reagent Co., Ltd., China). The chelate stock solution (2,500 mg/L) was prepared using [S,S]-ethylenediaminedisuccinic acid (S,S-EDDS, $C_{10}H_{16}N_2O_8$, Shandong Haohai Chemical Co., Ltd., China). The 719 strongly basic anion exchange resin (719 resin), γ-Al_2O_3, and AC were also used in our study. The characteristics of these engineering materials are briefly listed in Table 1.

2.2. Apparatus

A Metash UV-5200 UV–vis spectrophotometer (Metash, China) equipped with a quartz cuvette with a 1-cm path length was used to obtain adsorption spectra and absorbance measurements. Solution pH values were determined using a pB-10 pH meter (Sartorius, Germany). A shaker WHY-2 (Jshuanyu, China) was used to maintain the temperature and to obtain a stable suspended solution.

Table 1
Some characteristics of the adsorbents used in this study

Materials	719 resin	γ-Al_2O_3	AC
Manufacturer	Shanghai Resin Factory Co., Ltd	Zhengzhou Xinyida technology Co., Ltd	Tianjin Kemiou Chemical Reagent Co., Ltd
Appearance	Light yellow transparent spherical particles	White spherical particles	Black particles
Bulk density (g/mL)	0.68–0.74	0.52–0.68	0.38–0.45
Particle size (mm)	0.4–0.6	1.0–1.5	0.5–0.9
pH_{pzc} value	2.58	7.32	5.95

2.3. Adsorption experiments

We used S,S-EDDS to study the removal of copper ions by the three types of materials mentioned previously. The prepared solutions were composed of Cu(II): S,S-EDDS = 1:1 (molar ratio) and the characterization of S,S-EDDS and its complexes with heavy metal ions has previously been described by Kołodyńska [15].

For the adsorption isotherms and the kinetics studies, 0.2 g of adsorbent and 0.025 L of the Cu(II)–S,S-EDDS complex solution at different initial concentrations (25–175 mg/L) were added to 100-mL Erlenmeyer flasks. The contact time was varied from 10 min to 600 min. The suspensions were mixed in a thermostated shaker bath operating at 130 rpm for 10 h at room temperature. The mixture was filtered through a 45 μm filter membrane and the final concentration of Cu(II) in the filtrate was analyzed using a Metash UV-5200 spectrophotometer. The adsorption capacity q (mg/g) was calculated as follows:

$$q = (C_0 - C_e)\,V/m \tag{2}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of the Cu(II) ions, respectively, V (L) is the volume of solution, and m (g) is the weight of the adsorbents.

The pH values of the solutions were adjusted using 0.1 M NaOH and 0.1 M HCl. The effect of pH (3–7) on adsorption onto the 719 resin, γ-Al_2O_3, and AC was then determined. The experiments were conducted on the Cu(II)–S,S-EDDS complexes in a temperature range of 298–318 K.

3. Results and discussion

3.1. Effect of pH

The effect of pH on adsorption capacity was conducted over a pH range of 3.0–7.0. For Cu(II) the adsorption capacity is dependent on pH, as shown in Fig. 1. The adsorption capacity of the 719 resin showed a slight decrease from pH 3.0 to 4.0 after which (pH 4.0–7.0) it was almost constant, and nearly independent of solution pH. However, the adsorption capacities were dramatically reduced for γ-Al_2O_3 and AC with an increase in pH. We found a reduction in adsorption capacity for γ-Al_2O_3 (from 90.1 to 32.8%) and AC (from 70.9 to 36.8%) with an increase in pH from 3.0 to 7.0, respectively.

The pH_{pzc} values of the materials were determined using the salt titration method, as listed in Table 1. The surface charge of the sorbents was positive at $pH < pH_{zpc}$ because of excess protons on the surface, and negative at $pH > pH_{zpc}$. Cu(II) ions adsorbed strongly onto the 719 resin in the presence of S,S-EDDS with little sensitivity toward pH. This suggests that the adsorption of Cu(II) is unaffected by the degree of protonation for the 719 resin. Additionally,

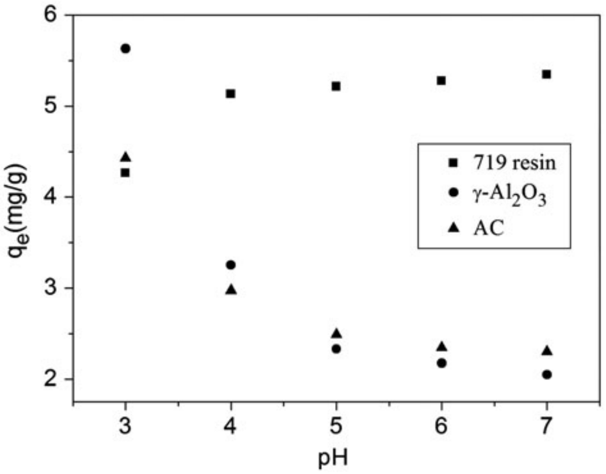

Fig. 1. Effect of pH on the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials (C_0 = 50 mg/L, T = 298 K).

γ-Al_2O_3 had a low adsorption capacity toward Cu(II)–S,S-EDDS at high pH values, indicating that negative charges were more prominent on γ-Al_2O_3, which rendered the Cu(II)–S,S-EDDS complex negative and the chelate hardly approached the γ-Al_2O_3 surface [18]. Wu et al. report similar behavior [19] as the adsorption of fulvic acid and Cu(II) onto γ-Al_2O_3 decreased at alkaline pH values. The adsorption capacity of AC in the presence of Cu(II)–S,S-EDDS decreased with an increase in pH. This is possibly related to the adsorption of Cu(II) being hindered at higher pH because of the electrostatic repulsion between negatively charged Cu(II)–EDDS complexes and the AC surfaces.

3.2. Effect of concentration

The initial concentration of the Cu(II)–S,S-EDDS solution was varied from 25 to 175 mg/L. The relationship between the amount of Cu(II)–S,S-EDDS complex adsorbed onto the 719 resin, γ-Al_2O_3, and AC, and the equilibrium concentration can be described by adsorption isotherms (Fig. 2). These data were used to verify the adsorption models and also to determine the real adsorption capacities. For the studied Cu(II)–S,S-EDDS complexes, the amount of adsorption increased with an increase in concentration until a plateau was reached. The theoretical maximum adsorption capacities determined using the above-mentioned conditions for the 719 resin, γ-Al_2O_3, and AC are 19.59, 6.05, and 6.66 mg/g for the Cu(II) complexes, respectively. The data are listed in Table 2 and are very similar to the experimental data shown in Fig. 2.

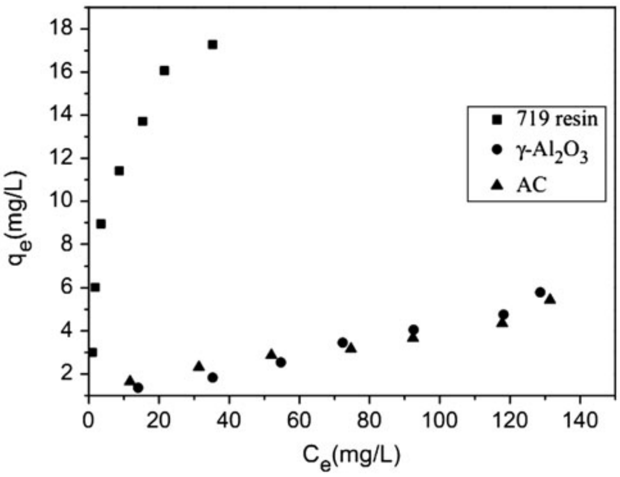

Fig. 2. Effect of initial concentration on the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials (pH 6.0, $T = 298$ K).

Isotherms are equilibrium relationships between the adsorbate concentration on the solid phase and its concentration in the liquid phase. To determine the adsorption mechanism, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models were used to analyze the experimental data.

3.2.1. Langmuir isotherm

The Langmuir isotherm model assumes monolayer adsorption onto a homogeneous surface and it can be expressed by the following equation [20]:

$$c_e/q_e = 1/K_{Lqm} + c_e/q_m \tag{3}$$

where c_e is the equilibrium concentration of Cu(II) ions, q_e (mg/g) is the amount of Cu(II) adsorbed per unit mass of adsorbent at the equilibrium concentration, q_m (mg/g) is the maximum adsorption capacity, and K_L (mL/mg) is the Langmuir constant, which is related to the adsorption energy. The Langmuir isotherm was applied to our experimental data and the results are shown in Fig. 3.

To describe the essential characteristics of the Langmuir isotherm, the equilibrium parameter R_L was defined by the following equation:

$$R_L = 1/(1 + K_L c_0) \tag{4}$$

where $R_L > 1$ indicates unfavorable adsorption, $R_L = 1$ indicates linear adsorption, $0 < R_L < 1$ indicates favorable adsorption, and $R_L = 0$ indicates irreversible adsorption. K_L is larger than zero (Table 2), $0 < R_L < 1$, which indicates that the adsorption process is favorable.

3.2.2. Freundlich isotherm

The Freundlich isotherm model can be used to describe the adsorption of multilayers and adsorption on heterogeneous surfaces [21]. It can be expressed by the following linear form:

$$\log q_e = \log K_F + \log C_e/n \tag{5}$$

where K_F and n are the Freundlich isotherm constants, which are related to the adsorption capacity and the intensity of the adsorbent, respectively. K_F and n were determined from a plot of log q_e vs. log C_e, as shown in Fig. 4. A value of $n > 1$ in Table 2 indicates that the adsorption conditions are favorable.

Table 2
Constants for the isotherm models for Cu(II)–S,S-EDDS adsorption by the three materials at 303 K

Adsorbent		719 resin	γ-Al_2O_3	AC
Langmuir isotherm	q_m (mg/g)	19.59	11.18	6.66
	K_L (L/mg)	0.193	0.007	0.017
	R^2	0.9923	0.5779	0.8012
Freundlich isotherm	K_F	3.99	0.21	0.51
	n	2.21	1.53	2.22
	R^2	0.8998	0.9403	0.9303
D–R isotherm	q_m (mg/g)	15.17	6.05	5.00
	K (mol^2/kJ^2)	1.446	450.748	285.041
	E (kJ/mol)	0.588	0.033	0.042
	R^2	0.7081	0.9122	0.6258
Temkin isotherm	K_T (L/g)	2.33	0.10	0.21
	b_T (J/mol)	627.03	1309.91	1830.37
	R^2	0.9887	0.8190	0.7893

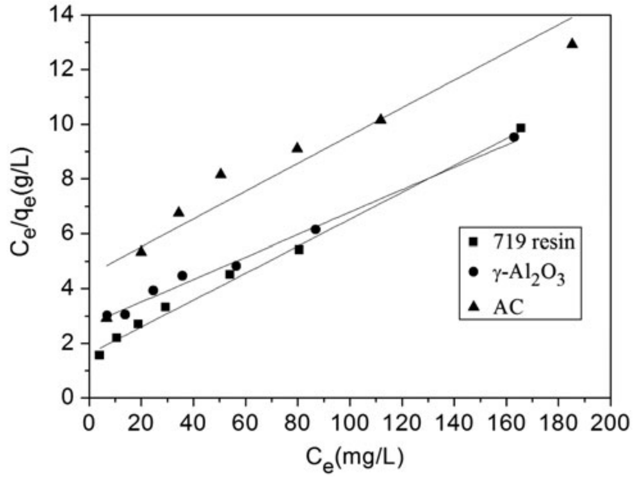

Fig. 3. Langmuir isotherm for the adsorption of Cu(II)–S, S-EDDS onto the three types of engineering materials.

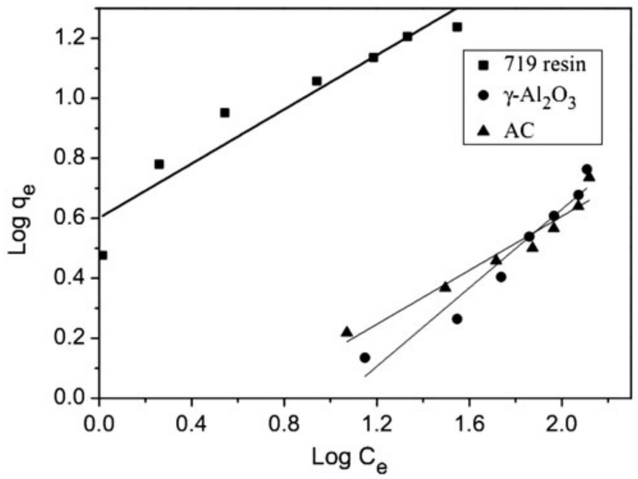

Fig. 4. Freundlich isotherm for the adsorption of Cu(II)–S, S-EDDS onto the three types of engineering materials.

3.2.3. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm can describe the adsorption mechanism and is based on a potential theory wherein a heterogeneous surface is assumed. It can be used to distinguish between the physical and chemical adsorption of metal ions on surfaces [22]. Its linearized form is given by the following equations [23]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{6}$$

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{7}$$

$$E = \frac{1}{\sqrt{-2K}} \tag{8}$$

where K is a constant related to the adsorption energy, and E (kJ/mol) is used to estimate the type of adsorption process. If $8 < E < 16$ kJ/mol, the adsorption process can be explained by an ion exchange mechanism whereas if $E < 8$ kJ/mol, a physical adsorption occurs [24]. A plot of $\ln q_e$ against ε^2 for Cu(II) ion adsorption onto the three types of engineering materials is shown in Fig. 5. It is clear that there is no linear fit between $\ln q_e$ and ε^2, however, the first five data points have a linear correlation and subsequently the Dubinin–Radushkevich isotherm parameters can be calculated from the slope of the line. As shown in Table 2, the calculated E values are 0.098, 0.070, and 0.051 kJ/mol for the 719 resin, γ-Al_2O_3, and AC, respectively, which indicates physisorption.

3.2.4. Temkin isotherm

The Temkin isotherm describes the behavior of heterogeneous surface adsorption systems and is expressed by the following equation [25]:

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \tag{9}$$

The linear form of the Temkin isotherm can be expressed by the following equations:

$$q_e = A + B\ln C_e \tag{10}$$

$$A = \frac{RT}{b_T}\ln K_T \tag{11}$$

$$B = \frac{RT}{b_T} \tag{12}$$

where R (8.341J/mol/K) is the gas constant, T (K) is the absolute temperature, A and B represent isotherm constants, K_T (L/g) is the equilibrium binding constant, and b_T (J/mol) is related to the heat of adsorption. A plot of q_e against ln C_e was used to calculate the constants, as shown in Fig. 6. It is clear then that the adsorption behavior of the 719 resin fits the Temkin isotherm well, which indicates that the heat of adsorption decreased linearly with temperature.

Table 2 shows the calculated parameters for all the isotherms and it can be concluded that the 719 resin has good correlation coefficients when using the Langmuir model and the Temkin isotherm, while γ-Al_2O_3 and AC have a better fit when using the Freundlich model.

3.3. Effect of contact time

The effect of contact time on the adsorption capacity of the Cu(II)–S,S-EDDS complexes on the 719 resin, γ-Al_2O_3, and AC is presented in Fig. 7. The removal was rapid for the 719 resin within the first 30 min, and the capacity reached about 4.90 mg/g, which was followed by a slower adsorption rate, and its adsorption capacity was found to be about 5.12 mg/g at equilibrium. The faster adsorption of the 719 resin suggests faster ion exchange between the chloride ions and the electronegative Cu(II)–S,S-EDDS as well as a higher affinity toward Cu(II)–S,S-EDDS ions by comparison with γ-Al_2O_3 and AC. For γ-Al_2O_3, the adsorption rate of Cu(II)–S,S-EDDS was fast in the first 2 h, and the capacity reached about 1.90 mg/g. The adsorption capacity increased slowly until the reaction reached equilibrium, and its capacity was about 2.23 mg/g. The internal diffusion of ions through the adsorbent is the limiting step in the γ-Al_2O_3 adsorption process. For AC, the adsorption rate increased quickly over the first 3 h after which a slight increase in the adsorption of copper was apparent. About 10 h was required to achieve equilibrium because the Cu species moved easily toward the AC surface, and they then migrated from the surface into the bulk. The migration speed slowed down and the adsorption took longer to reach equilibrium [15].

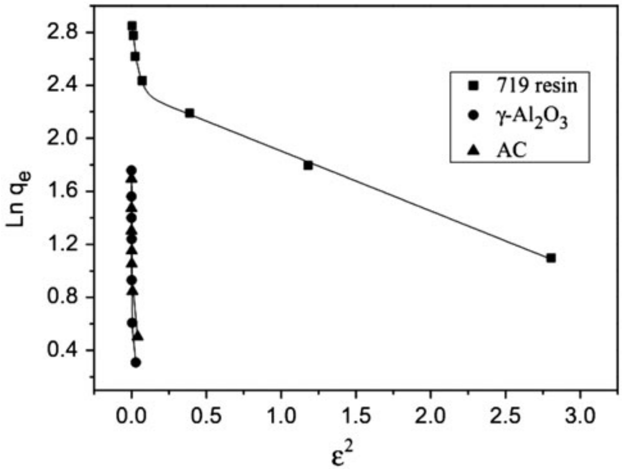

Fig. 5. D–R adsorption isotherm for the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials.

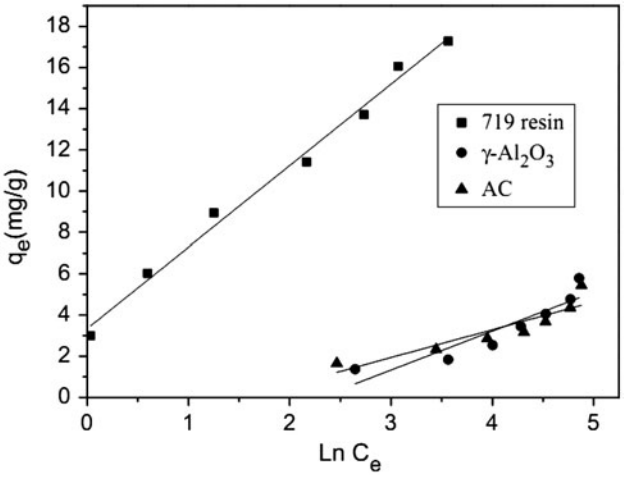

Fig. 6. Temkin adsorption isotherm for the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials.

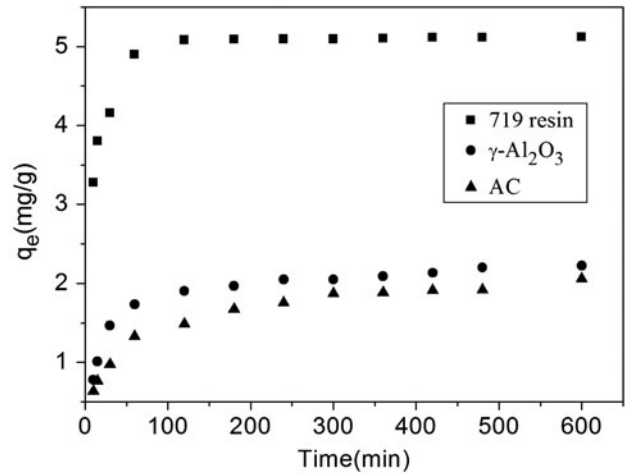

Fig. 7. Effect of contact time on the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials. (C_0 = 50 mg/L, pH 6.0, T = 298 K).

Adsorption kinetic models were used to investigate the adsorption mechanism and to determine the rate controlling step for Cu(II)–S,S-EDDS adsorption onto the three types of engineering materials studied. The rate constants were calculated using pseudo-first-order and pseudo-second-order kinetic models. The rate controlling step was also determined using an intraparticle diffusion model.

3.3.1. Pseudo-first-order model

The pseudo-first-order kinetic model is generally expressed by the following equation [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{13}$$

where q_e and q_t (mg/g) are the amount of Cu(II) ions adsorbed onto the three types of engineering materials at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the rate constant. A plot of log (q_e–q_t) against t was used to calculate k_1 and q_e, as shown in Fig. 8.

3.3.2. Pseudo-second-order rate model

The pseudo-second-order equation [27] can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

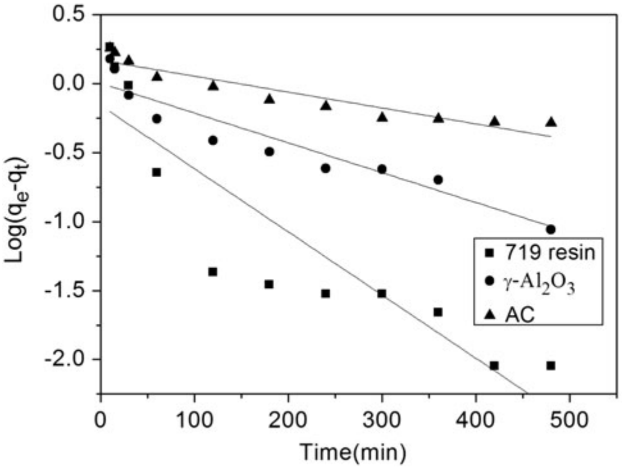

Fig. 8. Pseudo-first-order kinetics of Cu(II)–S,S-EDDS adsorption onto the three types of engineering materials.

where k_2 (g/mg/min) is the adsorption rate constant. The initial adsorption rate (h) (mg/g min) when $t \to 0$ can be determined using the following formula [28]:

$$h = k_2 q_e^2 \tag{15}$$

The values of k_2, q_e, and h can be determined by the plot of t/q_t against t, as shown in Fig. 9.

3.3.3. The intraparticle diffusion model

To determine the rate-limiting step, the intraparticle diffusion model was used together with the adsorption kinetics in the following equation [29]:

$$q_t = k_{id} t^{0.5} \tag{16}$$

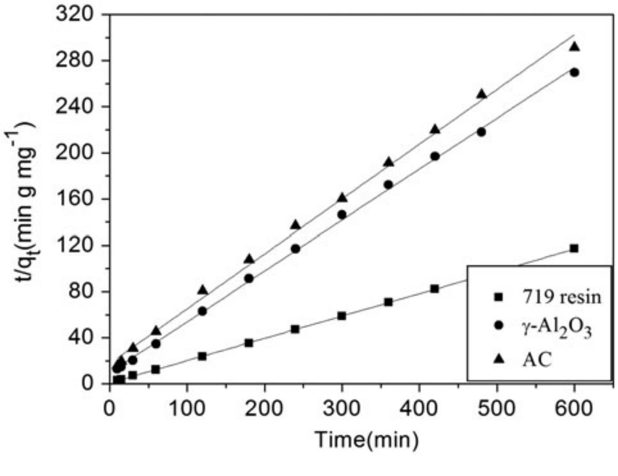

Fig. 9. Pseudo-second-order kinetics for Cu(II)–S,S-EDDS adsorption onto the three types of engineering materials.

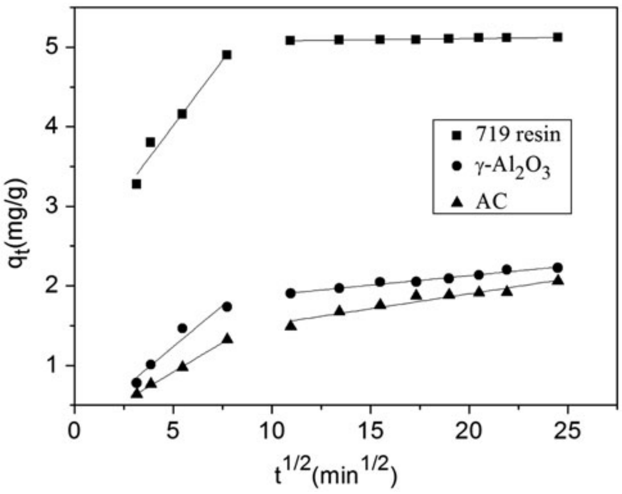

Fig. 10. Intraparticle diffusion for Cu(II)–S,S-EDDS adsorption onto the three types of engineering materials.

where q_t (mg/g) is the adsorption capacity at time t and k_{id} (mg/g min$^{-0.5}$) is the intraparticle diffusion rate constant. Plots of q_t against $t^{0.5}$ were used to determine k_{id}, as shown in Fig. 10.

Table 3 lists the kinetic parameters, rate constants, and adsorption capacities at equilibrium for Cu(II) ions at an initial concentration of 50 mg/L. The theoretical q_e values for the three types of engineering materials were close to the experimental q_e values from the pseudo-second-order kinetic model, which indicates that chemical adsorption was the rate-determining step. The theoretical q_e values calculated using the pseudo-first-order kinetic model deviated more from the experimental values than those from the pseudo-second-order kinetic model. Furthermore, the correlation coefficients (R^2) from the pseudo-first-order model were significantly lower than those from the pseudo-second-order model. These results show that pseudo-second-order kinetics better describe the data in this study.

Table 3
Kinetic parameters for the adsorption of Cu(II)–S,S-EDDS onto the 719 resin, γ-AlO$_3$, and AC

Kinetic equation	719 resin	γ-Al$_2$O$_3$	AC
q_e (exp)	5.12	2.23	2.06
Pseudo-first-order			
k_1 (min^{-1})	0.21	0.10	0.06
q_e (theor) (mg/g)	5.04	2.07	1.84
R^2	0.8022	0.8979	0.8767
Pseudo-second-order			
k_2 (g/mg/min)	4.33×10^{-2}	1.99×10^{-2}	1.27×10^{-2}
q_e (theor) (mg/g)	5.17	2.27	2.11
h	1.16	0.10	0.06
R^2	0.9999	0.9988	0.9964
Intra-particle diffusion			
k_{id}-1 (mg/g/min$^{-0.5}$)	0.33	0.21	0.15
R^2	0.9535	0.9258	0.9980
k_{id}-2 (mg/g/min$^{-0.5}$)	0.31×10^{-2}	2.43×10^{-2}	3.82×10^{-2}
R^2	0.9247	0.9713	0.9177

The plot of q_t against $t^{0.5}$ should be a straight line that passes through the origin when the rate-limiting step is intraparticle diffusion. However, the plots in Fig. 10 possess multi-linear portions, and this indicates that intraparticle diffusion is not the rate-limiting step. There are two straight lines that relate the data points and the three sharp, first-linear portions come from film diffusion. However, the three second-linear portions have some differences: the plateau portion of the 719 resin indicates an equilibrium state, and the two linear portions of γ-Al$_2$O$_3$ and AC are due to intraparticle diffusion. In Table 3, k_{id}-1 and k_{id}-2 refer to the first-linear portion rate constants and the second-linear portion rate constants, respectively. The correlation coefficients indicate a good fit for both portions.

3.4. Effect of temperature

The effect of temperature on the adsorption of Cu(II)–S,S-EDDS by the three adsorption materials was investigated between 298 K and 318 K (shown in Fig. 11). We found that the adsorption capacity (q_e) values of the three adsorption materials increased from 5.39 to 5.87, 2.03 to 2.22, and 2.13 to 3.67 (mg/g), respectively, as the temperature increased from 298 to 318 K. These slight changes could be due to the higher collision frequencies at higher temperature and hence enhanced adsorption. This also indicates that adsorption onto the three adsorption materials is endothermic [30].

Thermodynamic parameters such as the Gibbs energy changes (ΔG°), enthalpy changes (ΔH°), and entropy changes (ΔS°) were determined using the following equations [15,31].

$$K_C = \frac{q_e}{C_e} \tag{17}$$

$$\Delta G^\circ = -RT \ln K_C \tag{18}$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{19}$$

where K_C is the equilibrium adsorption constant, T is the absolute temperature (K) and R is the gas constant

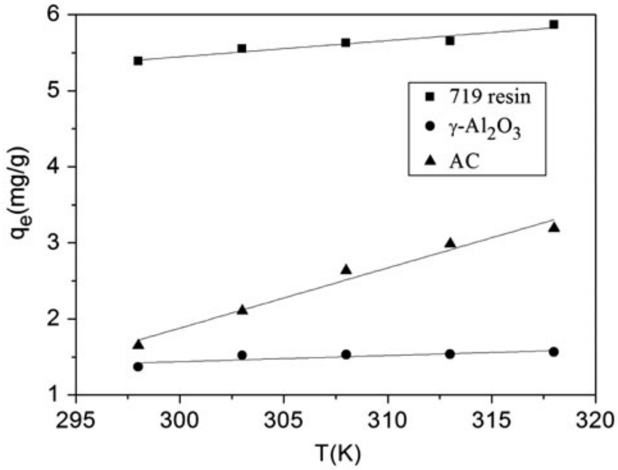

Fig. 11. Effect of temperature on the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials (C_0 = 50 mg/L, pH 6.0).

(8.314 J/K mol). Fig. 12 shows a plot of ln K_C vs. $1/T$ and the data can be fit to a straight line.

The Gibbs free energy changes (ΔG°) that were calculated using Eq. (18) for the different temperatures are listed in Table 4. The ΔH° and ΔS° values were calculated from the slope and the intercept of the linear regression by Eq. (19). It is clear from Table 4 that the ΔG° values for the 719 resin were positive at low temperatures (from 298 to 303 K) and became negative at higher temperatures (>308 K). The decrease in ΔG° values with an increase in temperature shows that the adsorption was favorable at higher temperatures. Furthermore, the ΔG° values for γ-Al_2O_3 and AC were negative at all the temperatures investigated, which indicates that the adsorption of the studied complexes is spontaneous. Positive ΔH° values indicate an endothermic Cu(II) adsorption process for the three types of engineering materials.c

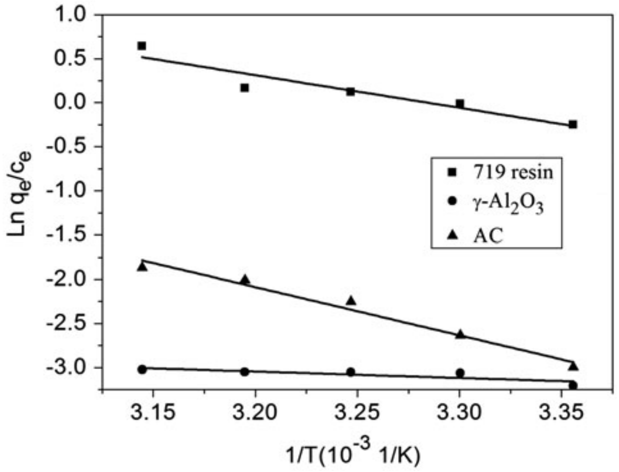

Fig. 12. Plot of ln k_c vs. $1/T$ for the adsorption of Cu(II)–S,S-EDDS onto the three types of engineering materials.

Table 4
Thermodynamic parameters for the adsorption of Cu(II)–S,S-EDDS at various temperatures onto the 719 resin, γ-AlO_3, and AC

T (K)	ΔG° (kJ° mol^{-1})	ΔS° (JK^{-1} mol^{-1})	ΔH° (kJ mol^{-1})
719 resin			
298	−0.615	101.07	30.77
303	−0.027		
308	0.306		
313	0.432		
318	1.701		
γ-Al_2O_3			
298	−7.944	−6.24	5.96
303	−7.715		
308	−7.824		
313	−7.939		
318	−7.998		
AC			
298	−7.419	128.20	45.48
303	−6.633		
308	−5.770		
313	−5.231		
318	−4.937		

4. Conclusions

Heavy metal Cu(II) ion adsorption in the presence of S,S-EDDS and onto the 719 resin, γ-Al_2O_3, and AC was studied in batch mode and their adsorption capacities were found to increase with an increase in phase contact time and the initial solution concentration. The absorption effectiveness was found to be nearly independent of solution pH on the 719 resin. On the contrary, the adsorption was strongly dependent on pH for γ-Al_2O_3 and AC. The adsorption isotherm data for the 719 resin in the Cu(II)–S,S-EDDS system fit the Langmuir and the Temkin isotherms well, as they provided the best correlation. The equilibrium parameter n from the Freundlich isotherm indicates that the adsorption of copper ions onto γ-Al_2O_3 and AC is favorable. The pseudo-second-order kinetic model agrees very well with the static data for Cu(II) in the presence of S,S-EDDS for its adsorption onto the three tested materials. The calculated E values are 0.098, 0.070, and 0.051 kJ/mol for the 719 resin, γ-Al_2O_3, and AC, respectively, which indicates a physisorption process. The adsorption efficiency of Cu(II) ions onto the three materials increased with an increase in temperature. Data obtained from the thermodynamic study at different temperatures were used to calculate the thermodynamic quantities. The results indicate that Cu(II) adsorption onto the 719 resin, γ-Al_2O_3, and AC is endothermic.

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