

## Adsorption of copper ions onto microwave stabilized heavy metal sludge

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### Abstract

Microwave stabilized heavy metal sludge was used as an adsorbent to remove the copper ions from aqueous solution. The adsorption characteristics of copper on the stabilized-sludge were studied by various models, such as Freundlich and Langmuir isotherm equation. Results show that the  $\text{pH}_{\text{zpc}}$  of stabilized-sludge was at 9.2–9.5. Moreover, the adsorption of copper ions onto the stabilized-sludge surface was mainly on account of the heterogeneous surface of the stabilized-sludge. In the dynamic study, the experimental data was fitted to the intraparticle diffusion model, pseudo-first order model and pseudo-second order model. However, the experimental data was only well correlated with pseudo-second order model with the correlation coefficient  $> 0.995$ .

Furthermore, both Freundlich and Langmuir isotherm equations were found to represent the measured adsorption data well. From the Langmuir equation, the adsorption capacity increased from 18 to 28 mg/g as the temperature rose from 15 to 55 °C, since this adsorption process was an endothermic reaction. After this adsorption process, copper ions can be concentrated on and in a small bead and recovery efficiently.

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### 1. Introduction

Heavy metal sludge produced by industrial wastewater treatment of printed circuit board plants is often regarded as a hazardous material. Copper ions in sludge are easy to leach out, and the concentration of metals often exceeds the legal criteria. Except for the metal ions, the heavy metal sludge also contains several salts:  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$  and insoluble metal hydroxide and  $\text{M}(\text{OH})_n$  [1]. In Taiwan, though copper ion in waste metal sludge is mostly treated with sulfuric acid and recovered by crystallization process, the leaching concentration of copper ions in the residual sludge under TCLP test still cannot meet the legal criterion (15 mg/L).

For years, microwave technique, offering the advantage of uniform and rapid heating, has been widely applied to the treatment of some environmental materials. These applications included heating and pyrolysis [2,3], extraction and digestion [4–10], synthesis [11–13] and sample preparation [14,15].

Moreover, the stabilization and immobilization of metal ions in soil and metal sludge through the microwave treatment are also reported [16–18]. This demonstrates that microwave treatment is quite efficient in inhibiting the leaching of metal ions from soil or sludge. Hence, the treated soil or sludge becomes a stable matrix for application.

For reducing the problems of metal ions in aqueous solution, many low-cost adsorbents have been used efficiently. These adsorbents include agricultural by-products [19–23], sewage sludge, metal hydroxide, soil minerals, etc. [24–27]. The reuse of these cheaper adsorbents for the adsorption of metal ions could achieve the goal of reclamation of solid wastes.

In this study, the adsorption of copper ions onto stabilized-sludge treated by microwave stabilization process was investigated. According to TCLP test, copper concentration in the raw sludge conformed to the legal criterion after the microwave stabilization process. Therefore, the microwave stabilization process-treated sludge was denominated as stabilized-sludge. The objectives of this research were to (1) investigate the chemical composition and surface characteristics of stabilized-sludge, (2) develop the kinetics relationship between copper ions and stabilized-sludge and (3) realize the influences of the

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initial pH and temperatures on adsorption of Cu onto stabilized-sludge.

## 2. Materials and methods

### 2.1. Sample preparation and characteristics

Raw heavy metal sludge came from Heavy Metal Sludge Treatment Plant, Tao-Yuan County, Taiwan, and had been handled by acid extraction process. However, according to toxic characteristics leaching procedure (TCLP, method 1311 published by USEPA) copper ion concentrations of the raw sludge, 33.10 mg/L, still exceeded the criteria of waste disposal in Taiwan, 15 mg/L.

In this study, the raw heavy metal sludge was first dried at 105 °C for 12 h at least until the moisture was removed and two successive weighting of sludge was maintained at a constant value within  $\pm 1\%$ . Then it was crushed with a grinder and sieved till the particle diameter ranged between 100 and 400 mesh (0.15–0.063 mm). The fine sludge was stored in a 20 L bucket with a plastic cover. Afterward the raw sludge was treated by microwave stabilization process that was established in previous study [18]. The operation parameters of microwave stabilization process are of power of 600 W, reaction time of 12 min, additive of 0.8 g Fe powder and liquid ( $H_2O$ ) to solid (sludge) ratio of 1. The TCLP test results showed that the copper ion of heavy metal sludge was “stabilized” through the microwave stabilization process with the leaching concentration of 1.04 mg/L. Hence, the stabilized-sludge was taken as the adsorbent in later adsorption experiment. Before performing the adsorption experiments, the stabilized-sludge was washed three times with a 0.01 M  $KNO_3$  solution at pH 7.2 adjusted by  $HNO_3$  and NaOH to remove debris and alkaline materials on the surface [28]. The washed-sludge was then frozen dried prior to storage.

Stock copper solution was prepared with distilled water and  $Cu(NO_3)_2 \cdot 3H_2O$  (reagent grade). The solution pH was adjusted with 0.1 M  $HNO_3$  and 0.1 M NaOH. The concentration of metal ions were analyzed by flame atomic adsorption spectrometer (FAAS).

The chemical composition of the raw heavy metal sludge was determined by modified microwave digestion method consulted from previous studies [5,29] with a microwave oven to quantify the metal contents. Samples of 0.1 g raw heavy metal sludge were well mixed with  $HNO_3$ –HCl–HF solution (3 mL individually) and two-stage programs of the microwave process were carried out. The first stage is 650 W for 10 min (final temperature 160 °C) and the second stage is 800 W for 15 min (final temperature 200 °C). After the microwave-assisted digestion process, the mixtures were cooled down to room temperature. The mixtures were also filtered and quantified to 50 mL before being analyzed. The same procedure was also followed for stabilized-sludge.

Surface charge,  $Q$  (mV), of the stabilized-sludge in the aqueous solution was measured at different pH values by Malvern Zetasizer 3000. Afterward surface charge measurements were plotted versus pH.

### 2.2. Adsorption kinetics experiment

In the kinetics experiments, different dosages (0.08, 0.1, 0.12 and 0.15 g) of stabilized-sludge were added to 100 mL of 30 mg/L copper solution in 250 mL flasks. The initial pH of the copper solution was adjusted at  $4 \pm 0.3$  with NaOH and  $HNO_3$ . The mixtures were then shaken in a temperature-controlled water bath at 120 rpm and  $25 \pm 1$  °C. At different desired contact times, the mixtures were taken and filtered using filter paper (0.5  $\mu m$ ) made by glass fiber. The remaining copper ion concentrations were then analyzed by FAAS.

Furthermore, several adsorption models have been applied to depicting the adsorption mechanism between adsorbent and adsorbate, such as the intra-particle diffusion model, pseudo-first-order kinetics model and pseudo-second order kinetics model. Each was discussed as follows.

Intra-particle diffusion model of Weber and Morris [33] is expressed as

$$Q_t = K_1 T^{1/2}. \quad (1)$$

The pseudo-first-order kinetic model of Lagergen [34] is

$$\frac{dQ}{dt} = K_1(Q_e - Q). \quad (2)$$

After definite integration by applying the initial condition  $Q_t = 0$  at  $T = 0$  and  $Q = Q_t$  at  $T = t$ , it can also be expressed as

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 T}{2.303}. \quad (3)$$

The pseudo-second order presented by Ho and McKay [36] is

$$\frac{T}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{T}{Q_e}, \quad (4)$$

where  $Q_t$  and  $Q_e$  represent the amounts of solute adsorbate per unit adsorbent (mg/g) at any time and at equilibrium, respectively. Furthermore,  $K_1$  is the intraparticle diffusion rate constant (mg/g min<sup>1/2</sup>) and  $K_1$  (1/min) and  $K_2$  (g/mg/min) are the rate constants of pseudo-first order model and pseudo-second order model, respectively. In addition,  $h = K_2 Q_e^2$  is the initial adsorption rate.

### 2.3. Effect of the initial pH

The effect of initial pH of the copper ion solution on adsorption was determined over a range of pH value 3–8. This experiment was performed with 0.1 g stabilized-sludge and 100 mL of 30 mg/L copper solution. The mixtures were shaken in the temperature-controlled water bath at 120 rpm and  $25 \pm 1$  °C until reaching equilibrium and the final pH and copper concentration of the solution were detected.

### 2.4. Isotherm study

Isotherm study of copper ions adsorbed onto the stabilized-sludge was carried out at different adsorbent dosages. The amounts of adsorbent were ranged from 0.08 to 0.3 g with

100 mL of 30 mg/L copper solution. The initial pH and temperature of the copper solution were  $4 \pm 0.3$  and  $25 \pm 1$  °C, respectively. The mixtures were shaken in 250 mL flasks at 120 rpm until the equilibrium time was reached. The equilibrium copper concentrations,  $C_e$  (mg/L), were analyzed and the amounts of copper adsorbed per gram of stabilized-sludge,  $Q_e$  (mg/g), were calculated. Similar individual isotherm experiments were also conducted at 15, 35, 45 and 55.

In the course of studying the adsorption isotherm of copper ions onto stabilized-sludge surface, the experimental data was fitted to the Freundlich and Langmuir isotherm equations.

The Freundlich sorption isotherm [37] is used in the linear form as

$$\log Q_e = \log k_F + \frac{1}{n \log C_e}, \quad (5)$$

where  $K_F$  (mg/g) and  $n$  (g/L) are the Freundlich constants, which are the adsorption capacity of the adsorbent and the symptom of the favorability of the adsorption process, respectively [35].

Moreover, the Langmuir sorption isotherm [38] has been widely applied to many adsorption processes and systems. The basic assumption of Langmuir adsorption is the monolayer adsorption on the adsorbent surface. It means no more adsorption of ions would occur at a non-active site, since the site was occupied by one ion. The Langmuir adsorption isotherm can be expressed as

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}, \quad (6)$$

where  $b$  and  $Q_0$  are the sorption equilibrium constant, which are the adsorption energy (L/g) and adsorption capacity (mg/g), respectively.

### 3. Results and discussions

#### 3.1. Characteristics of raw heavy metal sludge and stabilized-sludge

Microwave-assisted digestion was performed for the analysis of chemical compositions of raw heavy metal sludge and stabilized-sludge. As listed in Table 1, the major elements of raw heavy metal sludge and stabilized-sludge were Ca, Si, Fe, Cu and Al in decreasing sequence. The large amounts of Ca, Fe and Al may be attributed to the usage of lime, ferrous sulfate and poly-aluminum chloride, respectively, in wastewater treatment while the Cu and Si came from the process of printed circuit board treatment.

Fig. 1 illustrated the variation of surface charge of stabilized-sludge at different pH values. From the plot, the values of zeta potential were all below 0 mV in the studying pH range and it meant the negative charge was established on the surface of stabilized-sludge at the adsorption process. The negative charge of the surface may attribute to the high adsorption capacity of cationic ions by electrostatic attraction. Further, the  $pH_{zpc}$  of stabilized-sludge were much smaller than that of sewage sludge [25], for the existence of metal oxide and sulfide oxide resulted

Table 1  
Chemical composition of raw heavy metal sludge and stabilized-sludge

Element	Proportion (mg/g)	
	Raw sludge	Stabilized-sludge
Ag	0.15	N.D.
Al	12.24	3.47
Ba	0.92	N.D.
Ca	121.33	106.63
Cd	N.D.	N.D.
Co	0.11	N.D.
Cr	0.39	1.28
Cu	13.07	14.2
Fe	17.64	42.09
Ga	0.06	N.D.
K	2.49	1.84
Mg	1.89	0.84
Mn	0.27	N.D.
Ni	1.36	0.7
Pb	2.27	N.D.
Si	65.63	67.85
Zn	1.08	1.62

D.L. (detection limit) = 0.1 mg/L (0.025 mg/g) and N.D. means the concentration of metal ion is below detection limit.

from sulfuric acid extraction process and microwave stabilization process of raw sludge. On the contrary, results reported in the researches [30,31] indicated different phenomenon of adsorption of metal ions onto solid phase, goethite and  $Fe(OH)_3$ . In those studies, appreciable adsorption of cationic ions was at a pH value below the  $pH_{zpc}$ , even if the surface charge of the adsorbents was mostly positive. Hence, the difference between the stabilized-sludge and other solid adsorbent mentioned above on adsorption may result from the existence of other functional groups on other solid adsorbent.

Moreover, in Fig. 1, the surface charge declined steeply at the pH ranges of 2–4 and 8–10, but maintained around  $-25$  mV at the pH of 4–8, the pH interval in which the whole adsorption proceeded.

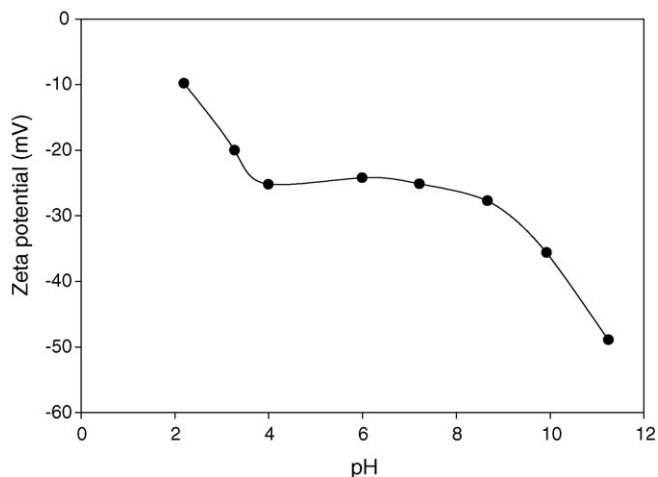


Fig. 1. Variation of surface charge of stabilized heavy metal sludge with system pH.

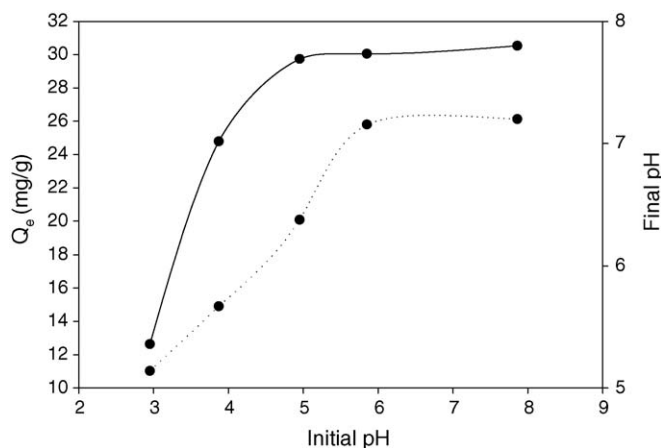


Fig. 2. The effect of initial pH on the adsorption of Cu(II) onto stabilized heavy metal sludge. (···) Initial pH vs. final pH. (—) Initial pH vs.  $Q_e$ .

### 3.2. Effect of the initial pH

In general, the pH values affect the species of heavy metals in the aqueous solutions, and the removal of heavy metals increases as the pH value rises. The pH value herein ranged from 3 to 8, and the surface charge of the stabilized-sludge also changed. From the calculation of solubility products ( $K_{sp}$ ), the formation of  $\text{Cu}(\text{OH})_2$ , the precipitating form, of 30 mg/L copper solution occurred as the pH value is beyond 6 [32]. As depicted in Fig. 2, the final pH was over 6 while the initial pH was above 5. Furthermore, the precipitation formed at pH 6, with the  $Q_e$  at the value of 29.7 mg/g (99% removal). On the other hand, the  $Q_e$  was around 23 mg/g when the final pH was 5.6 (initial pH at 4). This means that the decrease of copper ions in the solution does not only attribute to the formation of  $\text{Cu}(\text{OH})_2$ , but also the adsorption of copper ions on the stabilized-sludge surface at the studied pH range. However, at lower initial pH values, below 4, the influence of adsorption is responsible for the reducing of copper ions in the solution.

Also note that the final pH maintained at a constant of pH 7.2 as the initial pH was above 6, which played the role of buffer in this system. This suggests that the process is a suitable application on heavy metals removal because of its neutral and clean effluent.

### 3.3. Adsorption kinetics

Fig. 3 shows the relationship between contacting time and  $Q_t$ , the amount of solute adsorbed per unit adsorbent at any time. The curve rose steeply within the first 5 min, and  $Q_t$  reached a constant at the 60 min mark. Furthermore, from the preliminary study, a 12-h equilibrium experiment was performed. The equilibrium concentration of copper ions in this adsorption study did not vary obviously from 90 min to 12 h. Consequently, the equilibrium time of later adsorption experiments was therefore determined at the 90 min mark.

The relationships of  $Q_t$  versus  $T^{1/2}$  and  $\log(Q_e - Q_t)$  versus  $T$  for the intraparticle diffusion model and pseudo-first-order model expressed in Eqs. (1) and (3) of the adsorption of cop-

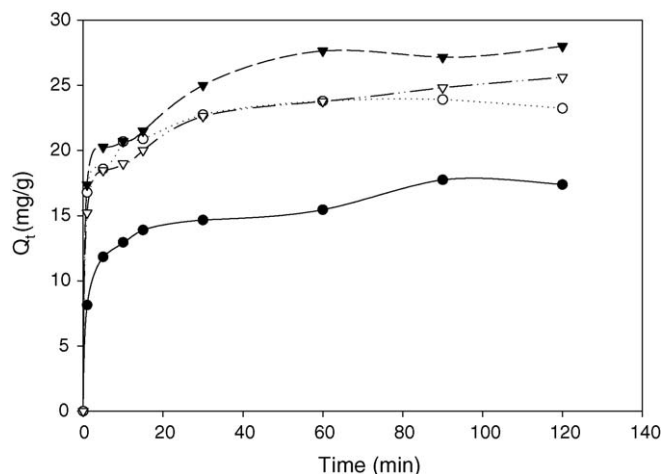


Fig. 3. The adsorption kinetics of Cu(II) ions onto stabilized heavy metal sludge (L/S = L/g). (●) 0.08 g, (○) 0.1 g, (▽) 0.12 g, (▼) 0.15 g.

per ions onto stabilized-sludge were plotted. From the linear regression analysis, the  $R^2$  value was 0.4983 for the former and 0.4942 for the latter for the initial concentration of 30 mg/L at 25 °C. These relationships were not illustrated herein owing to the lower correlation coefficient.

The relationship of  $T/Q_t$  versus  $T$  for the pseudo-second order kinetic model in Eq. (4) is demonstrated in Fig. 4. The result of linear regression analysis of this curve showed that the correlation coefficient  $R^2$  of the pseudo-second order model was greater than 0.995 at the equilibrium time of 120 min. This large agreement between experiment data and the pseudo-second-order model implied that, compared with the lower correlation coefficients of the first two models, the pseudo-second order kinetic model seemed to be more suitable for simulating the adsorption of copper onto stabilized-sludge surface. Moreover, for it also could be regarded as an activated sorption mechanism for chemical reaction was important and significant in the rate-controlling step [36].

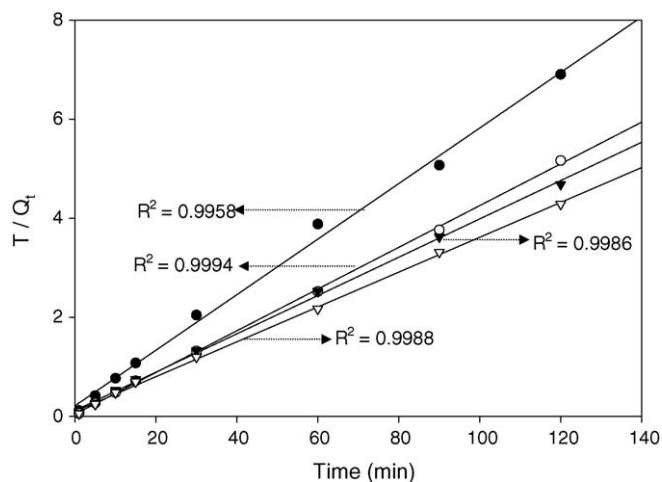


Fig. 4. Pseudo-second-order kinetics of Cu(II) ions absorption onto stabilized heavy metal sludge at 25 °C and initial pH  $4 \pm 0.3$ . (●) 0.08 g, (○) 0.1 g, (▽) 0.12 g, (▼) 0.15 g.

Table 2  
The calculated Freundlich and Langmuir constants and correlation coefficients at pH  $4 \pm 0.3$  and varying temperatures

Temperature (°C)	Freundlich			Langmuir		
	$n$ (g/L)	$K_F$ (mg/g)	$R^2$	$b$ (L/g)	$Q_0$ (mg/g)	$R^2$
15	14.86	15.22	0.9503	19.32	17.58	0.9993
25	15.06	18.78	0.9943	19.47	22.57	0.9981
35	12.82	20.06	0.9868	19.62	23.53	0.9998
45	10.81	22.58	0.9624	55.14	25.91	0.9994
55	9.11	24.86	0.9762	50.77	28.25	0.9990

Table 3  
Langmuir coefficients and thermodynamic parameters

Temperature (°C)	Langmuir		Thermodynamic parameters		
	$a$	$K_L$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)
15	17.18	83.1	-2.53	5.49	27.91
25	20.66	121.0	-2.84		
35	21.19	157.3	-3.09		
45	22.08	226.5	-3.43		
55	22.52	261.1	-3.63		

### 3.4. Adsorption isotherm

The adsorption isotherm study is basically essential when discussing an adsorption system. The data of adsorption isotherm for copper ions onto the stabilized-sludge at a constant temperature of 25 °C and initial concentration of 30 mg/L was listed in Table 2. It is also interpreted that the complete adsorption could not be reached at that situation for the  $Q_0$  behind 30 mg/g.

The  $K_F$  and  $n$  of Freundlich adsorption isotherm were determined from the plot of  $L_n Q_e$  (natural logarithm  $Q_e$ ) versus  $L_n C_e$  (natural logarithm  $C_e$ ) and  $Q_0$  and  $b$  of Langmuir adsorption isotherm can be calculated by the slope and intercept of  $C_e/Q_e$  versus  $C_e$  indicated which were listed in Table 2. The Langmuir adsorption capacity ( $Q_0$ ) was 22.57 mg/g at 25 °C, which was greater than many other solid wastes, such as tree fern, sewage sludge and herbaceous peat with the adsorption capacity of 10.6, 3.2–4.1 and 4.84 mg/g, respectively [19,25,35]. Furthermore, as the system temperature rose, the adsorption capacity ( $Q_0$ ) and  $b$  rose to about 17.58, 22.57, 23.53, 25.91 and 28.25 mg/g and 19.32, 19.47, 19.62, 55.14 and 50.77 L/g, respectively. These results imply that the adsorption capacity and intensity of copper ions onto stabilized-sludge were enhanced at higher temperatures, indicating clearly that that equilibrium of adsorption is temperature-dependent. This effect may be due to the fact that at higher temperatures, an increase in movement of the solute to adsorbent [39]. It also can be explained by the fact that the total energy of sorbate was increased with increasing temperature. Similar situations were displayed in other studies [19,26].

The effect of temperature also could be studied by some thermodynamic parameters, such as Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) determined with the following equations [24].

$$\Delta G^\circ = -RT \ln(K_L), \quad (7)$$

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (8)$$

where  $R$  is the universal gas constant (1.987 cal/mol/K),  $T$  is the temperature in Kelvin (K) and  $K_L$  is the Langmuir coefficient calculated from the following equation

$$Q_e = \frac{aK_L C_e}{1 + K_L C_e}. \quad (9)$$

The Langmuir coefficients,  $a$  (mg/g) and  $K_L$  (L/mg) can be obtained from the slope and intercept of  $1/Q_e$  versus  $1/C_e$  and  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of van't Hoff plots of  $\ln K_L$  versus  $1/T$  as listed in Table 3. The negative values of  $\Delta G^\circ$  at 15, 25, 35, 45 and 55 °C represent that the adsorption of copper ions onto stabilized-sludge is a spontaneous reaction. The positive value of  $\Delta H^\circ$ , 5.49 kJ/mol, indicates that the adsorption of copper/stabilized-sludge system belongs to endothermic reaction, which is similar to the result of Langmuir isotherm study in this research. Furthermore, depending to the positive and high value of entropy ( $\Delta S^\circ$ ), 27.91 J/mol/K, a higher randomness tendency between the interface of solid and aqueous phase exists in the process of adsorption. For the characters of spontaneous reaction, endothermic reaction and high randomness, the adsorption of copper ions onto stabilized-sludge may be enhanced at higher temperature.

### 4. Conclusion

The adsorption of copper ions onto stabilized-sludge was studied and leads to the following conclusions:

1. The surface charge of stabilized-sludge was whole negative at the pH range of 2–11, indicating the high adsorption capacity and affinity of metal ions onto stabilized-sludge.

2. The removal of copper ions increased as the initial pH rose, and the final pH maintained at a constant of pH 7.2 while the initial pH is from 6 to 8.
3. In the kinetic study, the adsorption of copper ions onto adsorbent was fitted to three kinetic models but only the pseudo-second order model was with great correlation coefficient ( $R^2 = 0.994$ ). This result shows the adsorption of copper ions onto stabilized-sludge to be an activated adsorption mechanism.
4. The experimental data was also analyzed by the Freundlich and Langmuir adsorption isotherm equations and the correlation coefficient of the Langmuir equation was better than the coefficient for the Freundlich equation.
5. In the isotherm experiment, both the  $Q_0$  and  $b$  increased as the temperature rose from 15 to 55 °C. This implies that the adsorption of copper ions onto stabilized-sludge was an endothermic reaction which can also be demonstrated by the thermodynamic study with the parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ .
6. The adsorption capacity of copper ions onto stabilized-sludge was around 23 mg/g, which was greater than that on many other solid wastes. Therefore, the stabilized-sludge seemed to be a good adsorbent on metal ions removal in aqueous solution.

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