

REMOVAL OF CADMIUM AND COPPER IN AQUATIC ENVIRONMENT BY MODIFIED KAOLINITE

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Abstract

The removal of Cd(II) and Cu(II) by kaolinite and its modified forms (by thermal or/and acid activation) in aqueous medium have been studied. Batch adsorption experiments were carried out with various pH values, interaction time and heavy metals concentration. The results showed that, the Cd(II) and Cu(II) adsorption of modified kaolinite was strongly affected by pH of medium. Initially, the rate of the adsorption was fast and then reached the maximum within 30 min of agitation for Cd(II) and Cu(II). The kinetic of adsorption was best described by second-order-mechanism. The amount of Cd(II) and Cu(II) adsorption at equilibrium, q_e , were 2.1-2.6 and 2.1-2.5 $\text{mg}\cdot\text{g}^{-1}$, respectively. The second-order rate constant, k , of Cd(II) and Cu(II) adsorption were 0.12-0.37 and 0.27-1.47 $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$, respectively. The adsorption data are good fit with Freundlich isotherm model. The Freundlich adsorption affinity were between 26.6 to 36.2 $\text{L}^n\cdot\text{mg}^{1-n}\cdot\text{kg}^{-1}$ for Cd(II), and between 6.7 to 14.4 $\text{L}^n\cdot\text{mg}^{1-n}\cdot\text{kg}^{-1}$ for Cu(II). The result indicated that kaolinite and its modified forms are good adsorbents for Cd(II) and Cu(II) in aqueous medium.

Keywords: Cadmium, copper, removal, modified kaolinite.

1. INTRODUCTION

Heavy metals (HMs) are considered as toxic pollutants in aquatic environment. In water environment, they have become a public health concern because of its non-biodegradable and persistent nature (Jiang *et al.*, 2009). Many projects have been studied on the removal of heavy metals from water and wastewater using different methods such as: chemical precipitation, ion exchange, solvent extraction, reverse osmosis and adsorption, etc. Reverse osmosis, although very effective, is a cost-prohibitive process because the membranes get easily spoiled, so they require a frequent replacement (Suraj *et al.*, 1998). Chemical precipitation is not very suitable when the pollutants presenting in trace amounts and also generating a large amount of sludge. Ion exchange is an expensive and complicated process. Solvent extraction or electrolytic processes are also available but they are cost-effective only for more concentrated solutions (Bhattacharya *et al.*, 2008b, 2008c). On the other hand, adsorption processes recognized as one of the preferred methods for

removing toxic elements from water because of their low cost, elimination of secondary pollutant generation, and the improvement of efficiency for treating water with low metal loading (Bhattacharya *et al.*, 2008a, Jiang *et al.*, 2009).

Clay minerals have different adsorption capacities for metal ions, which depend on adsorption condition. They have been found to be very effective, economical, versatile and simple (Jiang *et al.*, 2009). Kaolin is one of the plentiful natural clays in Vietnam. The main clay compositions of kaolin are kaolinites. There are many studies using raw kaolinite as an adsorbent for adsorption of some heavy metals such as Pb(II), Cd(II), Cu(II) and Ni (II) (e.g. Bhattacharya and Gupta, 2008a, 2008b, 2008c; Khai and Luyen, 2008; Jiang *et al.*, 2010). Typically, kaolinite has a low cation exchanged capacity and small specific surface area. Acid activation is one of the common techniques to improve the adsorption capacity of kaolinite (Khai *et al.*, 2010). Also, used kaolin clay can be the material for construction, pottery, porcelain. The present work studied the effects of medium factors on the adsorption of Cd(II) and

Cu(II) on kaolinite, which was modified by temperature or/and acid condition; the kinetics and adsorption isotherm.

2. MATERIAL AND METHODS

2.1. Material

Kaolin clay was collected from Vinh Yen, Vinh Phuc. In Vinh Yen, kaolin reserves of over 6 million tons. The clay sample was modified by method as describe elsewhere (Khai *et al.* 2010). The raw kaolin clay was used as control sample so named as M1; the acidic modified material is M2; the material which was thermal modified is M3; M4 is the kaolin sample which was thermal and acidic modified.

2.2. Batch adsorptions procedure

The experiments were carried out with the conditions in table 1. The mixture of adsorbent and HMs solution was shake, centrifuged (3000 rpm, 15 min), filtered and analyzed the HMs concentration in liquid phase by AAS (Atomic absorption spectroscopy).

Table 1: Experiment conditions

Experiment	Effect of pH	Kinetic adsorption studies	Isotherm adsorption studies
Material dosage (g)	1		
Interaction time (min)	60	5-180	60
pH	2.0-9.0 (Cd) 2.0-8.0 (Cu)	6.5 (Cd) 6.0 (Cu)	6.5 (Cd) 6.0 (Cu)
Initial HM concentration, mg L ⁻¹	50	50	40-180 (Cd) 10-50 (Cu)
Temperature, K	303		

2.2.1. Kinetic of adsorption

The kinetics of the adsorption process was studied at constant temperature using pseudo-first-order-model and pseudo-second-order-model for the rate expression. The first-order-model was given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Where k_1 is the first order rate constant, q_t and q_e are the amount of heavy metals adsorbed at time (t) and at equilibrium, respectively. After integrating (1) with the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, (1) may be rearranged for linearized data plotting as below:

$$\log(q_e - q_t) = \log(q_e) - k_1 \frac{t}{2.303} \quad (2)$$

The second-order-model was given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

By integrating (1) and using the boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, the linear form of the equation is obtained as

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (4)$$

The plot of (i) $\log(q_e - q_t)$ versus $\log(q_e)$ and (ii) t/q_t versus t give linear plots, which allows computation of the kinetic coefficients (Ho *et al.*, 1999).

2.2.2. Adsorption isotherm

The adsorption equilibrium is usually described by an isotherm equation which parameters express the surface properties and affinity of the adsorbents, at a fixed temperature and pH value. An adsorption process is usually described by the following two isotherms (Bhattacharyya and Gupta, 2008a):

(i) Freundlich isotherm:

$$q_e = K_f C_e^n \quad (5)$$

(ii) Langmuir isotherm:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t$$

Where C_e is the concentration of the adsorbate at equilibrium in the liquid phase, q_e is the corresponding concentration of the adsorbate in the solid phase, K_f and n are Freundlich coefficients. K_f represent an affinity constant ($L^n \text{mg}^{1-n} \text{kg}^{-1}$) and is numerically equivalent to the amount of metal adsorbed in mgkg^{-1} at a solution concentration of 1 mg L^{-1} . The regression constant, n , describes the non-linearity of the isotherm and provides information about the relative saturation of the adsorption sites. b and q_m are Langmuir coefficients which representing respectively the equilibrium

constant for the adsorbate-adsorbent equilibrium and the monolayer capacity.

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log q_e$ versus $\log C_e$ (ii) C_e/q_e versus C_e , respectively from which the adsorption coefficients could be evaluated.

3. RESULT AND DISCUSSION

3.1. Effect of pH

Fig. 1 shown the Cd(II) and Cu(II) adsorption onto clay materials when pH values increased. Generally, the HMs adsorption increased with increasing pH and reached plateau at $pH > 7$.

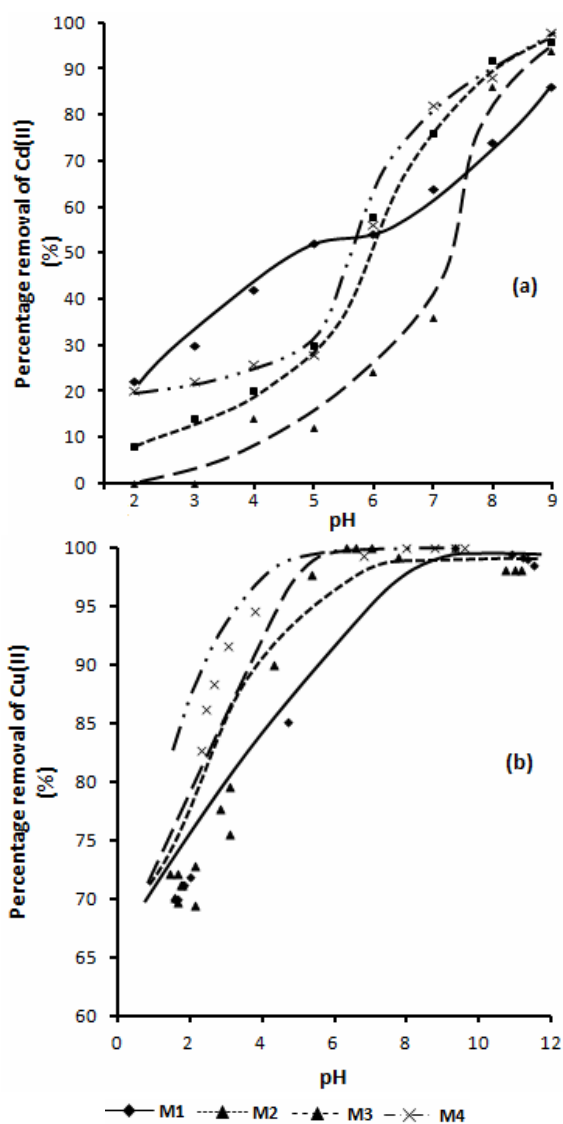


Fig 1: The dependence of percentage removal of Cd(II) (a), Cu(II) (b) in pH value

Similar trend was observed in many studies (Pagnanelli *et al.*, 2003; Chu, 2007; Bhattacharyya

et al., 2008; Jiang *et al.*, 2009, 2010). At low pH, the surface active sites of kaolinite may become positively charged, leading to decrease the adsorption affinity with HM cations in general. Besides, increasing the competition between large number of available H^+ and the metal ions for the available adsorption sites is also significantly affect factor. However, the more increase pH values are, the more increase the percentage of removed HMs. This trend can be explained by (i) the surface active sites become more negative charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction and (ii) the reducing of H^+ concentration. Jiang *et al.* (2010) stated that the active sites on the adsorbent surface are weakly acidic in nature and with increase in pH, they are gradually deprotonated favoring more Cu(II) uptake. The active sites on clay surface have been known to be weakly acidic and these sites are gradually deprotonated at higher pH resulting in larger uptake of HMs (Unuabonah *et al.*, 2008; Jiang *et al.*, 2010). At $pH > 7$, the precipitation of heavy metals also is involved in removal of them from solution.

3.2. Kinetic of adsorption

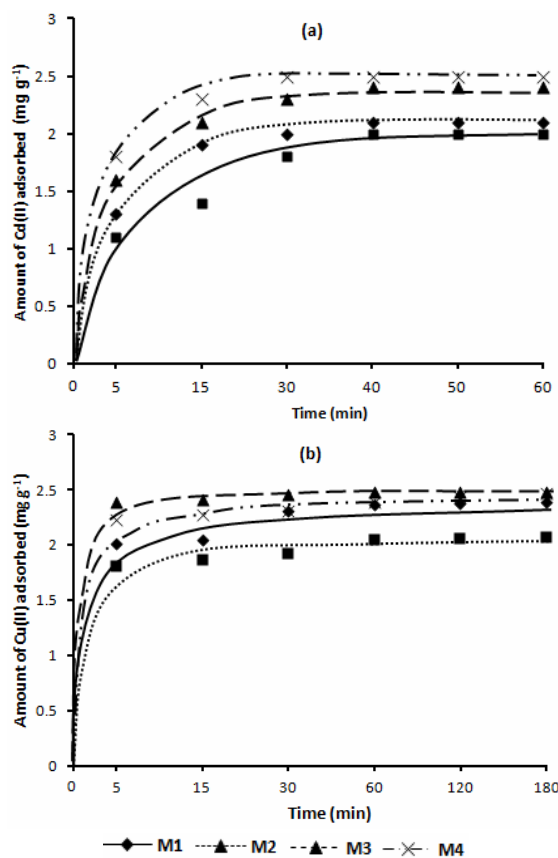


Fig 2: Various of amount Cd(II) (a) and Cu(II) (b) adsorbed per unit mass on clay at different interaction times

In the initial bare surface, the binding probability is high and consequently, adsorption proceeded with a high rate. By increasing coverage, the number of active sites becomes smaller and metal ions have to fiercely compete among themselves to be adsorbed. Together with this, the rate at which metal ions are transported from the bulk of the solution to the clay surface significantly affect the kinetics (Yu *et al.*, 2003). The amount of adsorption remained almost constant due to the decrease of adsorption sites on the clays which gradually interacted with the metal ions. The adsorption rate, on another hand depends on the metal ions which transported from the bulk liquid phase to the actual adsorption sites (Yu *et al.*, 2003).

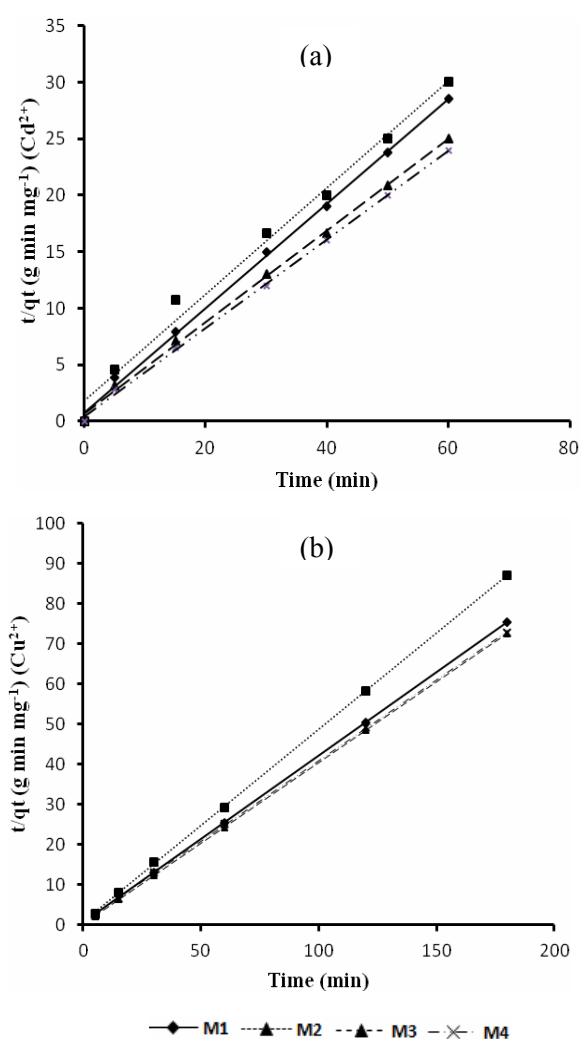


Fig. 3: Linear plots of second-order model for Cd(II) (a) and Cu(II) (b) adsorption

In the present work, pseudo-first order equation and second-order equation were tested to find out which model is in agreement with the experimental results of kinetic study.

Figure 2 showed the HMs adsorption data at various contacting times. Obtained data gave poor fits with the pseudo-first-order model but very good fits with the pseudo-second-order model at all reaction times. Figure 3 showed a linear regression of t/q_t with time, t for all the clay samples. The initial sorption rate h , pseudo-second-order rate constant k , amount of metal ions adsorbed at equilibrium q_e obtained from the pseudo-second-order model are given in table 2.

The initial sorption rate h of M4 is the highest, 2.40 with Cd^{2+} and $9.05 \text{ mg g}^{-1} \text{ min}^{-1}$ with Cu^{2+} , the one of M2 is the lowest, 0.50 with Cd^{2+} and $1.32 \text{ mg g}^{-1} \text{ min}^{-1}$ with Cu^{2+} . The amount of metal ions adsorbed at equilibrium, q_e , follow this trend with M4 showing the highest value of 2.55 and 2.48 mg.g^{-1} for Cd^{2+} and Cu^{2+} adsorption, respectively. The q_e values obtained from experimental were also good fit with the q_e obtained from the second order plot.

Modifying kaolinite clay thermal and acid activated tends to increase initial sorption rate h , especially thermal treatment follow by acid activation. Generally, there was an observed by decrease in the pseudo-second-order rate constant, k , for adsorption of metal ions on both modified kaolinite and unmodified kaolinite, except M3, the thermal modified kaolinite. This trend indicates that the modification with acid decreased the time for the adsorption of Cd(II) and Cu(II) to reach the equilibrium. This was also indicated in previous research (Khai *et al.*, 2010). The linearity of the plots of the pseudo-second-order model in Fig. 3 illustrates that chemical reaction rather than physisorption is the main rate-controlling step throughout most of the adsorption process and that the mechanism follows a pseudo-second-order reaction scheme.

Table 2: Second-order kinetic coefficient of Cd(II) and Cu(II) adsorption

Samples	R ²	q _e mg g ⁻¹	k g mg ⁻¹ min ⁻¹	h mg g ⁻¹ min ⁻¹
Cd(II)				
M1	0.98	2.12	0.12	0.55
M2	0.99	2.16	0.26	1.22
M3	0.99	2.46	0.24	1.47
M4	0.99	2.55	0.37	2.40
Cu(II)				
M1	0.99	2.41	0.27	1.56
M2	0.99	2.08	0.30	1.32
M3	0.99	2.48	0.25	1.56
M4	0.99	2.48	1.47	9.05

3.3. Adsorption isotherm

The adsorption isotherms of Cd²⁺ and Cu²⁺ adsorbed by raw and modified kaolin samples are shown in figure 4. From the adsorption curves, we presumed that the adsorption followed Freundlich isotherm. The adsorption affinity coefficient (K_f) was determined from Eq. (5). Also the relationship coefficient R^2 is high ($R^2 > 0.9$), which means that the adsorption isotherm is good fit with the Freundlich isotherm.

Table 3: The Freundlich coefficients of kaolin samples with Cd(II) and Cu(II) adsorption

Freundlich coefficients	M1	M2	M3	M4
	Cd			
K_f	26.56	25.42	16.64	36.22
n	0.53	0.56	0.67	0.47
R^2	0.98	0.94	0.97	0.99
Cu				
K_f	6.73	6.38	10.54	14.37
N	0.85	0.8	0.91	0.86
R^2	0.97	0.99	0.99	0.98

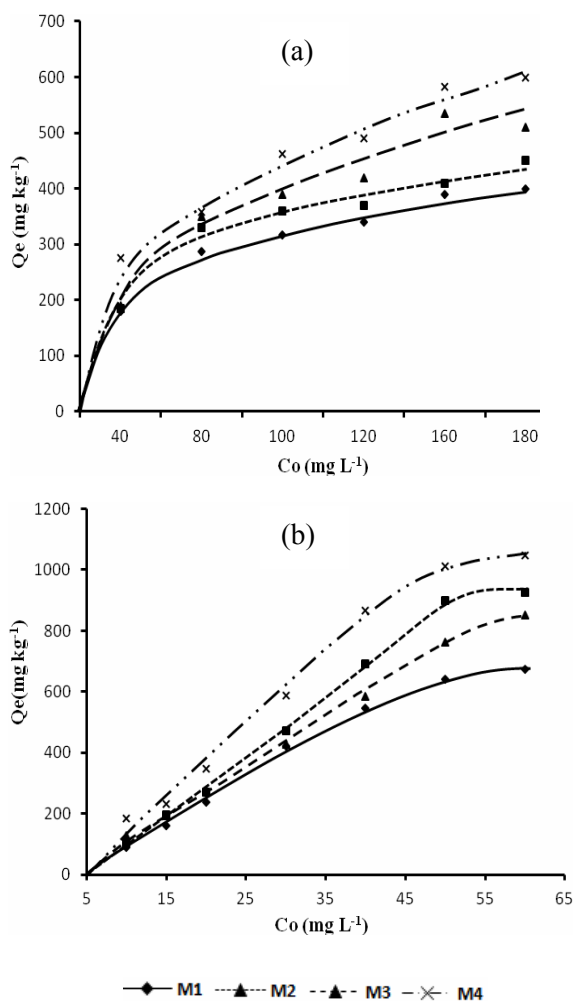


Fig. 4: Plots of initial HMs concentration C_0 and at equilibrium q_e of Cd(II) (a) and Cu(II) (b) adsorption on kaolin samples

A plot of $\lg q_e$ versus $\lg C_e$ yields a straight line with slope $1/n$ and the interception $\lg K_f$ as shown in Fig. 5. The Freundlich coefficient of kaolin samples with Cd(II) and Cu(II) adsorption are shown in table 3.

The adsorption affinity of kaolinite samples is 26.56-36.22 and 6.73-14.37 $L^n \text{mg}^{1-n} \text{kg}^{-1}$ for Cd(II) and Cu(II), respectively. The adsorption capacity of M4 is highest with K_f of 14.37 and 36.22 $L^n \text{mg}^{1-n} \text{kg}^{-1}$ for Cd(II) and Cu(II), respectively, which suggests that the modification by thermal and acid can significantly the removal of Cd(II) and Cu(II). The constant n is < 1 (or $1/n > 1$), that suggests a decrease sorption energy with increasing saturation of the exchangeable sites. Therefore the mechanism of this process could be the chemical adsorption.

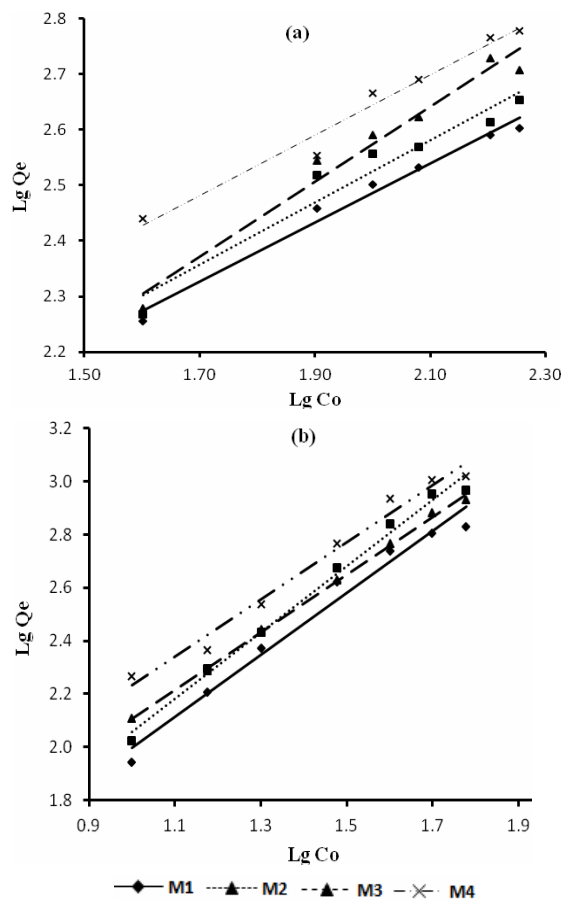


Fig. 5: Linear plots of Freundlich isotherm of Cd (a) and Cu (b) adsorption at 303 K

According to the Freundlich adsorption isotherm, we can determine the amount of adsorbent required to remove a certain pollutant by the following equation:

$$\frac{m}{V} = \frac{K_f}{C_0 - C} \quad (7)$$

Where m is the amount of adsorbent (g), V is volume of water (L), C_0 is concentration of heavy metal in, C is the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$) at adsorption capacity a ($\text{mg}\cdot\text{g}^{-1}$) of adsorbent. The amount of adsorbents are required to treat Cu(II) and Cd(II), to the concentration acceptable by the regulation of HMs concentration guiding of QCVN 08:2008/BTNMT (level A1) are shown in table 5.

Table 5: Adsorbent dosage (mg) per volume of solution (L) to remove Cd(II) and Cu(II) to achieve the regulation of HMs concentration guiding of QCVN 08:2008/BTNMT (level A1)

	C_0 , mg L^{-1}	C , mg L^{-1}	K_f , $\text{L}^n\text{mg}^{1-n}\text{kg}^{-1}$	n	m/V , mg L^{-1}
Cd					
M1	50	0.005	26.56	0.53	31.21
M2	50	0.005	25.42	0.56	38.22
M3	50	0.005	16.64	0.67	104.58
M4	50	0.005	36.22	0.47	16.65
Cu					
M1	50	0.1	6.73	0.85	109.37
M2	50	0.1	6.38	0.8	139.57
M3	50	0.1	10.54	0.91	57.61
M4	50	0.1	14.37	0.86	50.44

As shown in table. 5, the amount of clays for adsorption of Cd(II) is from 16.65 to 104.58 $\text{g}\cdot\text{m}^{-3}$ and Cu(II) is 50.44 to 139.57 $\text{g}\cdot\text{m}^{-3}$. For treatment of both Cd(II) and Cu(II), M4 is the least amount. Amount of M4 in adsorption of Cd(II) and Cu(II) are about 16.7 and 50.5 $\text{g}\cdot\text{m}^{-3}$, which are as half less as required amount of M1. According to the results, the modification by thermal and acid activation increasing the adsorption capacity of kaolin samples for treatment Cd(II) and Cu(II), reducing requirement of adsorbent mass, operation cost, required adsorbent dosage.

4. CONCLUSIONS

Adsorption of Cd(II) and Cu(II) on the kaolin clays is influenced by pH of the medium. It can be seen that more and more metal ions are taken up by

the clays as pH is increased. But at $\text{pH} > 7$, the precipitation of the heavy metal ions are detected to be involved in the removal of them from solution. Kinetics of adsorption are fitted with pseudo-second-order model at all reaction times. The adsorption data are good fit with Freundlich isotherm model. According to the results, the modification kaolin with acid follow with thermal has increased the adsorption capacity of clays for Cd(II) and Cu(II), also reduced contact time of adsorbent. This indicated the potential of modified kaolin about treatment the wastewater, especially HMs.

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