KKU Res. J. 2012; 17(5):800-810
http : //resjournal.kku.ac.th

# Adsorption of lead, cadmium and copper on natural and acid activated bentonite clay

*Supattra Budsaereechai, Khanita Kamwialisak and Yuvarat Ngernyen**

*Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University,*
*Khon Kaen, 40002, Thailand*
**Correspondent author: nyuvarat@kku.ac.th*

## Abstract

The aim of this research work was to prepare acid activated bentonite clay by using HCl as an acid chemical reagent. The adsorption capacity of natural and acid activated bentonite clay with lead, cadmium and copper was also investigated. Concentrations of the metals were analysed by using flame atomic absorption spectrophotometry. All specific surface area of natural and acid activated bentonite clay was measured by $N_2$ adsorption. The results showed that acid activated clay increased its specific area with 57% of $S_{BET}$ (47 to 74 $m^2/g$), while the average pore diameter of acid activate bentonite clay was smaller than that of natural bentonite clay. The maximum adsorption capacity of natural and acid activated bentonite clay were found to $Pb^{2+}$ with 83.02 and 92.85 mg/g, respectively, followed by $Cd^{2+}$ and $Cu^{2+}$. The Langmuir adsorption model could be used to explain the adsorption isotherm with the pseudo-second order. However, the uptake sorption data of all metals was more similar with pseudo-first order than that of pseudo-second order.

**Keywords**: bentonite clay, adsorption, lead, cadmium, copper

## 1. Introduction

Heavy metals were extensively known of difficulty to eliminate. The biological treatment could not be applied to treat effluent water with metal contaminants due to their inhibitory ability on bacteria in the system (1). The physical and chemical treatment has been used in metal effluent removal. The adsorption method with different types of adsorbent has been used to treat these metals from wastewater (2-5). Many types of clay have been reported of their high capability in adsorption (4). Bentonite clay is alumina-silicate clay mineral, which has been used, in metal absorption because of its physicochemical properties i.e. large specific area, high cation exchange capacity and strong absorptive affinity with organic and inorganic substances, low cost and low permeability. Many research works have used natural bentonite clay as an adsorbent to eliminate metals from water. The chemical activation, such as NaCl and KCl, has been used to improve specific surface area of natural bentonite. However, no much work has utilised HCl to activate natural bentonite. HCl is strong acid to be able to improve specific surface of natural clay.

There are many studies on the adsorption of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$. For example, Zou et al. (6) studied the adsorption of $Pb^{2+}$ and $Cu^{2+}$ from aqueous solutions using manganese oxide coated zeolite. Goyal et al. (7) and Chen and Wu (8) investigated the adsorption of $Cu^{2+}$ using activated carbon. In the study of Demirbas et al. (9), Amberite IR-120 synthetic sulfonated resin was used to adsorb $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$. However, the use of these adsorbents is restricted due to high costs. Therefore, it is relevance to find suitable low cost adsorbent. Thus, the objective of this work is to understand the adsorption capacity of natural and acidic bentonite with different metals (lead, cadmium and copper). The kinetic adsorption of both natural and acidic bentonite with three metals will also be investigated.

## 2. Materials and Methods

### 2.1 Materials

The bentonite clay was obtained from Thai Nippon Chemical Industry Co., Ltd. The chemical and physical properties of bentonite clay are given in Table 1 (the data obtained from Thai Nippon Chemical Industry Co., Ltd.). Silica and alumina are their major constituents along with traces of sodium, magnesium, calcium, potassium and titanium oxides as impurities.

**Table 1.** Chemical and physical properties of bentonite clay.

| Chemical compound (on dry basis) | % |
|---|---|
| Silicon dioxide ($SiO_2$) | 46-60 |
| Aluminum oxide ($Al_2O_3$) | 14-17 |
| Ferric oxide ($Fe_2O_3$) | 6-8 |
| Sodium oxide ($Na_2O$) | 0.5-1.5 |
| Magnesium oxide (MgO) | 1.5-3.0 |
| Calcium oxide (CaO) | 1.0-2.5 |
| Potassium oxide ($K_2O$) | 0.1-1.0 |
| Titanium dioxide ($TiO_2$) | 0.2-1.5 |
| Loss on ignition (LOI) | 7-12 |
| Moisture content | 8-12 % |
| Dry particle size | Min. 75% pass through 200 mesh |

The acid activated bentonite clay was prepared by using HCl. The clay was soaked with HCl at ambient temperature with ratio 1:50. Then it was shaken at 120 rpm for 24 h. The sample was then separated and washed with distilled water.

### 2.2 Surface analysis

The porous properties of the natural and acid activated bentonite clay were determined from $N_2$ adsorption isotherm data at -196°C with an automated adsorption apparatus (ASAP 2010, Micromeritics). The specific surface area ($S_{BET}$) and micropore volume ($V_{mic}$) were calculated using the Brunauer-Emmet-Teller (BET) method and Dubinin-Radushkevich (DR) equation (10), respectively. The total pore volume ($V_T$) was found from the amount of $N_2$ adsorbed at relative pressure = 0.99. The mesopore and macropore volume ($V_{meso+mac}$) was obtained by subtraction of the micropore volume from the total pore volume. The average pore diameter ($D_p$) was calculated from $(4\times V_T)/S_{BET}$.

### 2.3 Adsorption studies

A stock solution of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$ was prepared by dissolving $Pb(NO_3)_2$, $Cd(NO_3)_2.H_2O$ and $Cu(NO_3)_2$ in distilled water, respectively. The adsorption of natural and acid activated bentonite clay was carried out in a batch system. To find the time for the adsorption to equilibrium, 1 g of clay was added to 50 mL of metal solution with a concentration of 2000 mg/L. The mixture was shaken (120 rpm) for 6-48 h at ambient temperature. The metal concentration was analyzed by using flame atomic absorption spectrophotometer (Analysis 100, Perkin Elmer).

The amount of heavy metal adsorption per unit weight of clay at time $t$ ($q_t$) (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{1}$$

where $C_o$ and $C_t$ are the metal concentrations (mg/L) at the beginning and time $t$, respectively. $V$ is the volume of the metal solution and $W$ is the weight of clay.

Adsorption isotherms of the heavy metals were determined by varying the initial concentration of the metal solutions in range of 100-5000 mg/L at ambient temperature with equilibrate time.

## 3. Results and Discussion

### 3.1 Characterization of the samples

Figure 1 shows the nitrogen adsorption-desorption isotherms measured on natural and acid activated bentonite clay. It can be seen that both samples shows type IV adsorption isotherms based on IUPAC's classification (11) and a large uptake is observed near saturation pressure. The porous properties were determined from the conventional analysis of nitrogen isotherm as shown in Table 2. According to the definition by IUPAC, it can be seen that the natural and acid activated bentonite clay samples are mesoporous adsorbent pores with average diameter in a range of 2-50 nm. Anyway, the adsorbent pore ($D_p$) of activated clay was smaller than those of natural clay, while the specific surface area ($S_{BET}$) and the total pore volume ($V_T$) was more than that of nature clay, this could be the effect of the acid activation. The similar result has been reported elsewhere (12).

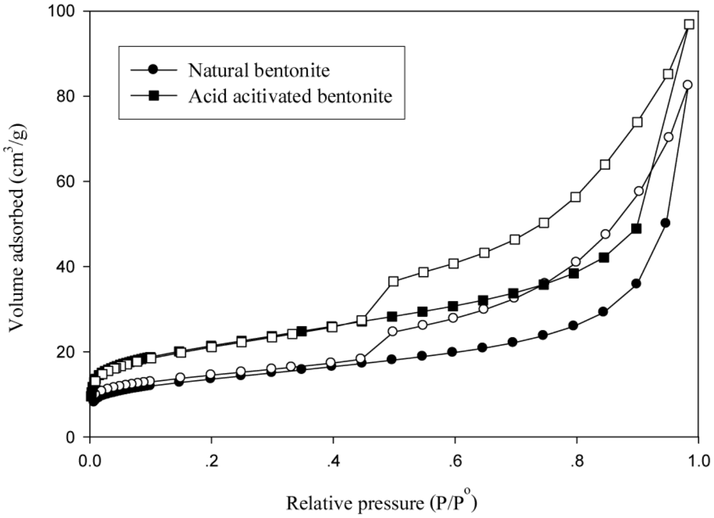

**Figure 1.** Adsorption (closed symbol) and desorption (opened symbol) isotherms of $N_2$ at -196°C onto the natural and acid activated bentonite clay.

**Table 2.** Porous properties of the natural and acid activated bentonite clay.

| Sample | $S_{BET}$ (m²/g) | $V_{mic}$ (cm³/g) | $V_{meso+mac}$ (cm³/g) | $V_T$ (cm³/g) | $D_p$ (nm) |
|---|---|---|---|---|---|
| Natural bentonite | 47 | 0.02 (15%) | 0.11 (85%) | 0.13 | 10.9 |
| Acid activated bentonite | 74 | 0.03 (20%) | 0.12 (80%) | 0.15 | 8.1 |

### 3.2 Kinetic studies

The results of the kinetic experiments of adsorption of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$ with natural bentonite clay are shown in Figure 2. The rapid adsorption observed during the first 12 h is probably due to the abundant availability of active sites on the clay surface. The adsorption of all three metals reached equilibrium within 36 h. Therefore, a time of 36 h was suitable for the study of the adsorption isotherm of all three metals. The maximum adsorption was observed on $Pb^{2+}$ with ca. 75 mg/g while $Cu^{2+}$ had the lowest adsorption on clay with ca. 25 mg/g. However, the atomic weights of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$ were 207.2, 106.42 and 63.545 g/g mole, respectively. The amounts of all metals were uptaken in a range of 0.37-0.40 mmole atom/g of natural clay, indicating that the natural clay was unselectively adsorbed to any of the metals. Similar result was reported by Liu and Zhou (13). However, the adsorption capacity of $Cu^{2+}$ in this work was higher than that of Liu and Zhou's work.

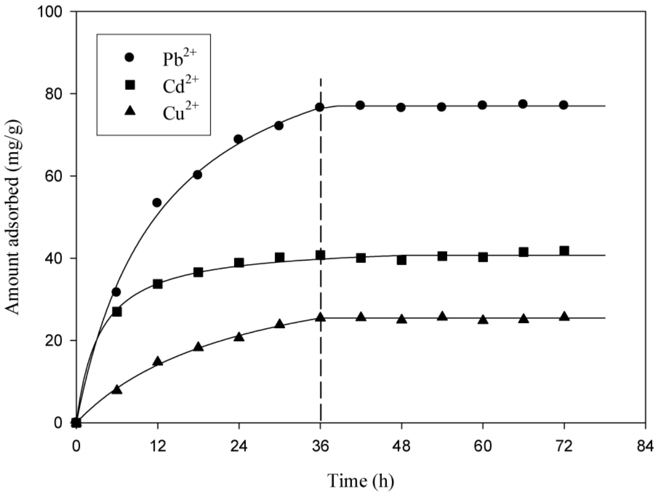

**Figure 2.** Adsorption of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$ onto natural bentonite clay as a function of time at ambient temperature (initial concentration 2000 mg/L).

The rates of adsorption were determined by pseudo-first order and pseudo-second order kinetics models. The pseudo-first order kinetic model (14) was expressed as:

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

where $q_e$ and $q_t$ were the amounts of metal adsorbed on clay (mg/g) at equilibrium and at time *t*, respectively, and $k_1$ was the rate constant of pseudo-first order adsorption ($h^{-1}$). The slopes and intercepts of plots of $\log(q_e - q_t)$ versus *t* were used to determine the pseudo-first order rate constant $k_1$ and $q_e$.

The pseudo-second order kinetic model (15) was expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where $k_2$ (g/mgh) was the rate constant of pseudo-second order adsorption. The slopes and intercepts of plots of $t/q_t$ versus *t* were used to calculate $k_2$ and $q_e$.

Figure 3 (a) and (b) present the plots of the pseudo-first order and pseudo-second order kinetics of the adsorption of the metals on natural bentonite clay. The calculated kinetic parameters were given in Table 3. The coefficients of determination ($R^2$) of the three metals obtained from pseudo-second order model (0.971-0.998) were higher than there in the pseudo-first order model (0.958-0.995). Thus, the adsorption kinetics were fitted better with the pseudo-second order kinetic model. Similar result was reported by Liu and Zhou (13) who reported that the kinetic adsorption of $Cu^{2+}$ and $Ni^{2+}$ could be fitted with pseudo-second order. However, the uptake sorption data of all metals from experiment was more similar with pseudo-first order than that of pseudo-second order.

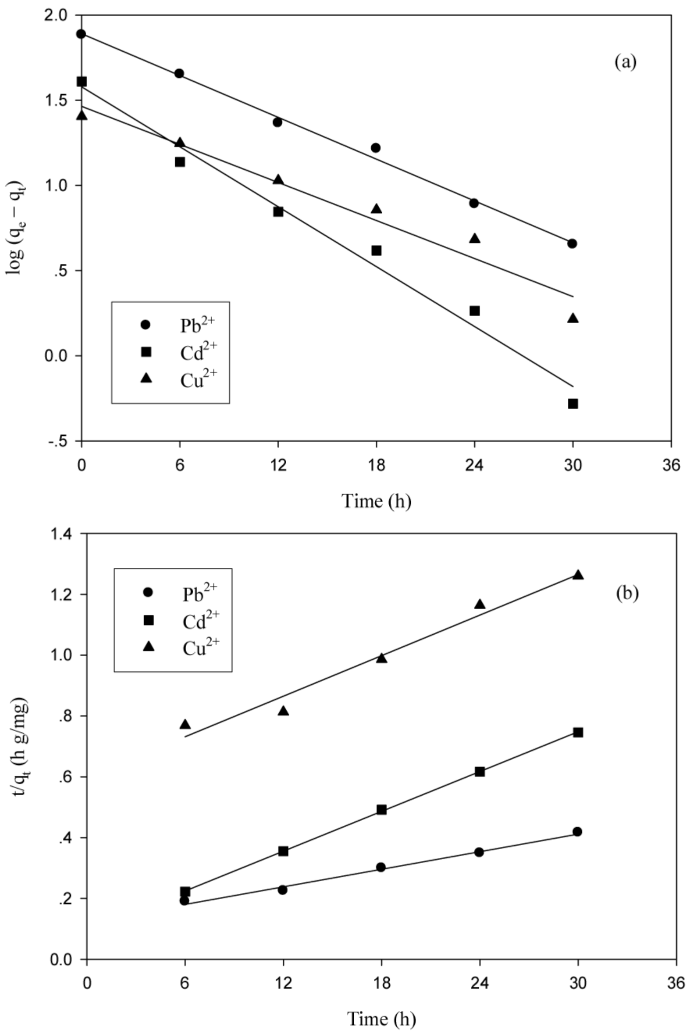

**Figure 3.** Adsorption kinetic for adsorption of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$on natural bentonite at ambient temperature (initial concentration 2000 mg/L) (a) pseudo-first order and (b) pseudo-second order.

**Table 3.** Adsorption parameters of kinetic for the adsorption of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$ on natural bentonite clay.

| Metal ion | $q_{e,exp}$ (mg/g) | Pseudo-first order | | | Pseudo-second order | | |
|---|---|---|---|---|---|---|---|
| | | $q_e$ (mg/g) | $k_1$ ($h^{-1}$) | $R^2$ | $q_e$ (mg/g) | $k_2$ (g/mg h) | $R^2$ |
| $Pb^{2+}$ | 76.5 | 77.67 | 0.094 | 0.995 | 103.89 | $7.54´10^{-4}$ | 0.998 |
| $Cd^{2+}$ | 41.5 | 37.86 | 0.135 | 0.983 | 45.86 | $5.06´10^{-3}$ | 0.999 |
| $Cu^{2+}$ | 25.4 | 29.12 | 0.086 | 0.958 | 44.99 | $8.26´10^{-4}$ | 0.971 |

### 3.3 Equilibrium studies

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Figure 4, Figure 5 and Figure 6 show the plots of amounts adsorbed versus equilibrium concentrations for the adsorption isotherms of $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$, respectively, on the natural and acid activated bentonite clay. It can be seen that the adsorption capacity of both clays is in proportion with metal concentrations. The sorption ability of metals were in the following order: $Pb^{2+} > Cd^{2+} > Cu^{2+}$.

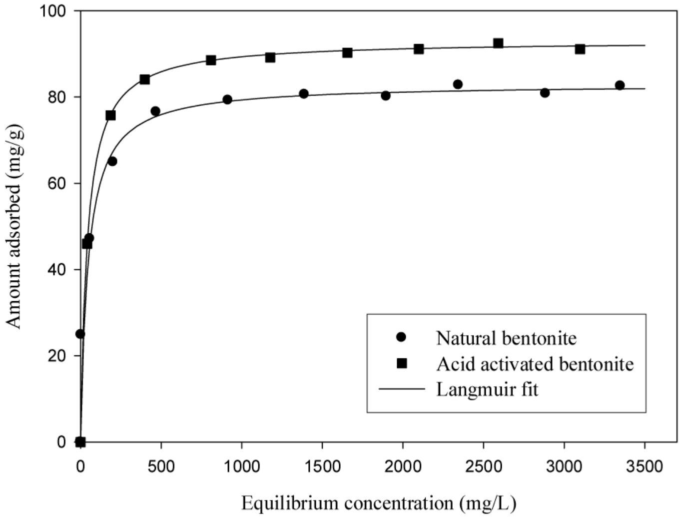

**Figure 4.** Adsorption isotherm of $Pb^{2+}$ on the natural and acid activated bentonite clay at room temperature (initial concentration 100-5000 mg/L)

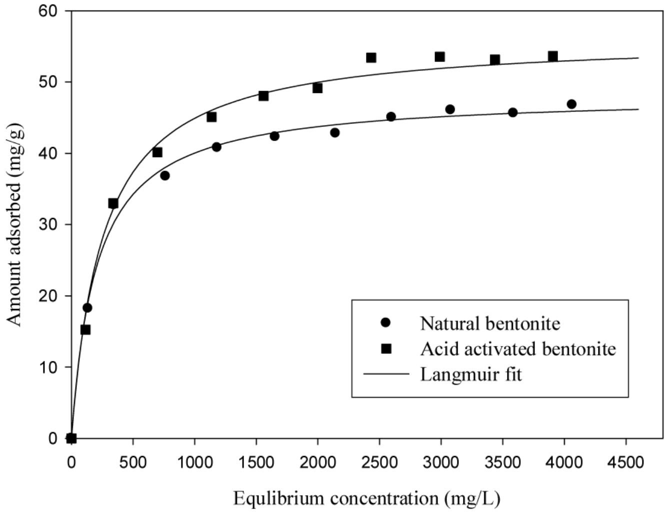

**Figure 5.** Adsorption isotherms of $Cd^{2+}$ on the natural and acid activated bentonite clay at room temperature (initial concentration 100-5000 mg/L).

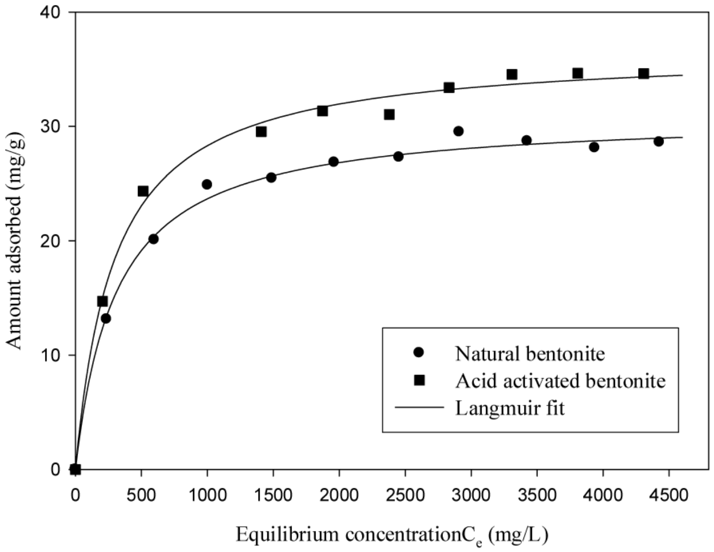

**Figure 6.** Adsorption isotherms of $Cu^{2+}$ on the natural and acid activated bentonite clay at room temperature (initial concentration 100-5000 mg/L).

Furthermore, the results clearly shown that acid activation clay has higher sorption capacity than that of natural clay. This could be effect of HCl activation on its surface as mentioned in section 3.1. The uptake adsorptions of all metals were increased with 11.8% for $Pb^{2+}$, 20.08% for $Cd^{2+}$ and 18.36% for $Cu^{2+}$.

It has been known that the adsorption system of components from liquid phase onto a solid phase is commonly explained by Langmir isotherm model (16). The adsorption isotherms plotted in Figure 4-Figure 6 were fitted to the Langmuir equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the amount adsorbed at equilibrium (mg/g), $q_m$ is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g) and $K_L$ is the Langmuir constant (L/mg). The values of the Langmuir equation's parameters are given in Table 4. High values of $R^2$ (> 0.98) for all three metals indicate good agreement between experimental and predicted data using the Langmuir equation.

**Table 4.** Fitting parameters of the Langmuir equation.

| **Metal ions** | **Sample** | **$q_m$ (mg/g)** | **$K_L$ (L/mg)** | **$R^2$** | **$R_L$** |
|---|---|---|---|---|---|
| $Pb^{2+}$ | Natural bentonite | 83.02 | 0.021 | 0.988 | 0.009-0.322 |
| | Acid activated bentonite | 92.85 | 0.023 | 0.999 | 0.009-0.303 |
| $Cd^{2+}$ | Natural bentonite | 48.20 | 0.005 | 0.982 | 0.038-0.667 |
| | Acid activated bentonite | 57.88 | 0.003 | 0.991 | 0.062-0.769 |
| $Cu^{2+}$ | Natural bentonite | 30.99 | 0.003 | 0.988 | 0.062-0.769 |
| | Acid activated bentonite | 36.68 | 0.003 | 0.983 | 0.062-0.769 |

The essential characteristics of Langmuir equation can be expressed in term of a dimensionless separation factor $R_r$, which is defined as

$$R_L = \frac{1}{1+K_L C_o} \qquad (5)$$

where $C_o$ is the initial metal concentration (mg/L) and $R_L$ values indicate the shape of the isotherm. The nature of the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). $R_L$ values obtained are also listed in Table 4. All the $R_L$ values for the adsorption of all three metal onto natural and acid activated bentonite clay shows that the adsorption process favorable.

Table 5 shows the uptake capacity of natural and acid activated bentonite clay in this work comparing with some adsorbents in the literature. Promisingly, the high adsorption capability of untreated and treated bentonite clay onto all metals was shown over different types of absorbent. This demonstrated the potential of this clay in many application field, including wastewater treatment. However, different results may be obtained from different operational parameters.

**Table 5.** Adsorption capacities of clays and some other adsorbents for $Pb^{2+}$, $Cd^{2+}$ and $Cu^{2+}$.

| **Adsorbent** | **$Pb^{2+}$ (mg/g)** | **$Cd^{2+}$ (mg/g)** | **$Cu^{2+}$ (mg/g)** | **References** |
|---|---|---|---|---|
| Natural bentonite | 83.02 | 48.20 | 30.99 | Present study |
| Acid activated bentonite | 92.85 | 57.88 | 36.68 | Present study |
| Untreated Tunisian Clay | 25.44 | - | - | (12) |
| Sulfuric acid Tunisian Clay | 40.75 | - | - | (12) |
| Na-bentonite | - | - | 17.88 | (13) |
| | - | - | 26.00 | (17) |
| Ca-bentonite | - | - | 12.00 | (17) |
| Clinoptilolite | 27.70 | - | 25.76 | (2) |
| Peat | - | 5.16 | 7.39 | (3) |

## 4. Conclusion

The acidic activation clay showed higher specific surface area than that of the natural clay. The maximum absorption capacity of acidic bentonite clay was ca. 92.85 mg of $Pb^{2+}$/g of bentonite. The natural and activation clay was also unselectively adsorbed to with any metals. Furthermore, a Langmir isotherm model could be used to explain the absorption kinetic with pseudo-second order reaction.

## 5. Acknowledgement

The authors are grateful to the Thai Nippon Chemical Industry Co., Ltd. for kindly supplying bentonite clay. This work was supported by Khon Kaen University.

## 6. References

(1) Lipczynska-Kochany E, Kochany J. Effect of humate on biological treatment of wastewater containing heavy metals. Chemosphere 2009; 77: 279-84.

(2) Sprynskyy M, Buszewski B, Terzyk AP, Namiesnik J. Study of the selection mechanism of heavy metal ($Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Cd^{2+}$) adsorption on clinoptilolite. J. Colloid Interface Sci. 2008; 304: 21-8.

(3) Liu Zr, Zhou Lm, Wei P, Zeng K., Wen Cx, Lan Hh. Competitive adsorption of heavy metal ions on peat. Journal of China University of Mining and Technology 2008; 18: 255-60.

(4) Sdiri A, Higashi T, Hatta T, Jamoussi F, Tase N. Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems. Chemical Engineering Journal 2011; 172: 37-46.

(5) Zhao X, Jia Q, Zhou W. Adsorption of zinc (II), cadmium (II), and copper (II) with PTFE Selective resin containing primary amine N1923 and Cyanex925. Korean J. Chem. Eng. 2009; 26: 1729-32.

(6) Zou W, Han R, Chen Z, Jinghua Z, Shi J. Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode. Colloids and Surface A: Physicochemical and Engineering Aspects 2006; 238-46.

(7) Goyal M, Rattan VK, Aggarwal D, Bansal RC. Removal of copper from aqueous solutions by adsorption on activated carbon. Colloids and Surface A: Physicochemical and Engineering Aspects 2001; 229-38.

(8) Chen JP, Wu S. Simultaneous adsorption of copper ions and humic acid onto an activated carbon. J. Colloid Interface Sci. 2004; 208: 334-42.

(9) Demirbas A, Pehlivan E, Gode F, Altun T, Arslan G. Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberite IR-120 synthetic resin. J. Colloid Interface Sci. 2005; 282: 20-5.

(10) Do DD. Adsorption Analysis: Equilibria and Kinetics. London: Imperial College Press; 1998.

(11) Rouquerol F, Rouquerol J, Sing K. Adsorption by Powders and Porous Solids. London: Academic Press; 1999.

(12) Eloussaief M, Benzina M. Efficiency of natural and acid-activated clays in the removal of Pb(II) from aqueous solutions. J. Hazard Mater. 2010; 178: 753-57.

(13) Liu Zr, Zhou Sq. Adsorption of copper and nickel on Na-bentonite. Process Safety and Environmental Protection 2010; 88: 62-6.

(14) Ho YS, McKay G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research 2000; 34: 735-42.

(15) Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochemistry 1999; 34: 451-65.

(16) McKay G, Blair HS, Gardner JR. Adsorption of dyes on chitin. I. Equilibrium studies. Journal of Applied Polymer Science 1982; 27: 3043-57.

(17) Ding Sl, Sun Yz, Yang Cn., Bh. Removal of copper from aqueous solutions by bentonites and the factors affecting it. Mining Science and Technology (China) 2009; 19: 489-92.