

REMOVAL OF Cd²⁺ FROM AQUEOUS SOLUTION BY ADSORPTION USING MONTMORILLONITE

Permpoon Ekboon, Pronpan Sansupan, Chakkrit Umpuch*

Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Ubonratchathani 34190, Thailand

**E-mail: Jaggrit@hotmail.com*

Abstract

In this study, montmorillonite clay has been utilized as the adsorbent for the removal of a heavy metal, cadmium, from aqueous solution by the batch adsorption technique under different conditions of initial cadmium concentration, solution pH, temperature, and contact time. Attempts were made to fit the isothermal data using Langmuir and Freundlich equations. The experimental results have demonstrated that the equilibrium data are fitted well by a Freundlich isotherm equation. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were considered to evaluate the rate parameters. The experimental data fitted the pseudo-second-order kinetic model. The results indicate that montmorillonite clay, which is produced commercially in Thailand, adsorbs cadmium efficiently and could be employed as a low-cost alternative in wastewater treatment for the removal of cadmium.

Keywords: *Montmorillonite, Cd²⁺, adsorption*

1. Introduction

Cadmium is typical environmental heavy metal pollutant. It is toxic and presence in different wastewater sources such as mining, smelting, electrolyzing, painting, alloying, electroplating, textile processing and printing. It can be accumulated in living organisms, causing health problems in human beings, plants and animals. Thus it is necessary to treat the heavy metal to reduce the concentration before discharge.

Traditional method for the removal and recovery of cadmium form industrial waste water are precipitation, ion exchange, electrolysis, adsorption on activated carbon [1-3]. However, many techniques which have been used had its drawback and shortcoming. Using large amounts of reagent and production of second pollution is flaw of precipitation method while high cost is the main problem of the ion exchange method, membrane separation method and adsorption method by activated carbon.

Clays have been increasingly paid attention to use as adsorbents because they are cheaper than other materials such as activated carbon and zeolite. Clay linings have been used as barriers in landfills to prevent contamination of groundwater and subsoil by leachates containing metals [4]. Montmorillonite is the layered mineral which composes of three sheets which is an octahedral sheet and two tetrahedral sheets. There is interlayer as barrier between each layer. The octahedral sheet consists of M₂₋₃(OH)₆ (where M is typically Al³⁺), which is situated between two SiO₄ tetrahedral ones[5]. The net charge on the clay surfaces resulting from the replacement of Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ or Zn²⁺ for Al³⁺ in the octahedral layer. Naturally, exchangeable cations such as H⁺, Na⁺, or Ca²⁺ offset the charge imbalance on the layer surfaces. The interlayer space can be expanded in aqueous solution because water is intercalated into the interlamellar space of montmorillonite. Montmorillonite can absorb heavy metals via two different mechanisms: (1) cation exchange in the interlayers

resulting from the interactions between ions and negative permanent charge and (2) formation of inner-sphere complexes through Si-O⁻ and Al-O⁻ groups at the clay particle edges [6-7]. Both mechanisms are pH and temperature dependent. It is interesting to examine the knowledge of the effect of pH and temperature on the sorption capacity of montmorillonite in soil-solution system.

Thus this study, alternative adsorbent such as montmorillonite clay has been utilized as the adsorbent for the removal of Cd²⁺ from aqueous solution by the batch adsorption technique under different condition such as initial Cd²⁺ concentration, amount of adsorbent, solution pH, temperature, and contact time.

2. Materials and Methods

2.1 Clays and reagents

Montmorillonite clay was obtained from Thai Nippon Chemical Industry Co. Ltd. The cation exchange capacity (CEC), data from the supplier, is 80 meq. per 100g of montmorillonite. The chemical composition of the montmorillonite clay used is shown in Table 1. As can be seen in Table 1, SiO₂ and Al₂O₃ are the major constituents of the clay with other oxides present in much smaller amounts.

Table 1 Chemical composition of montmorillonite clay

Component	Weight (%)
SiO ₂	55 – 58
Al ₂ O ₃	16 – 18
Fe ₂ O ₃	5 – 7
Na ₂ O	3.6 – 4.0
MgO	2.1 – 2.5
CaO	1.9 – 2.1
K ₂ O	0.3 – 0.5
TiO ₂	1.2 -1.5
LOI	11 – 12

A cadmium solution used, analytical grade, was prepared from concentrated stock solutions (Merck Titrisol).

2.2 Adsorption studies

In order to determine Cd²⁺ adsorption isotherm, 0.2g of clay sample was mixed well with 200 mL of different concentration of Cd²⁺ ranging from 20 to 100 mg L⁻¹ in 500 mL Erlenmeyer flask. The flask with samples were shaken overnight at 35 °C and then centrifuged at 35000 rpm for 1hr. The concentration Cd²⁺ in the supernatant was determined by an atomic adsorption spectrophotometer. The amount of Cd²⁺ adsorbed on the clay was calculated from the balance relationship.

The effect of pH and temperature on Cd²⁺ sorption was also investigated. The initial solute concentration of Cd²⁺ was 100 mg L⁻¹. The pHs of the suspensions were adjusted to around 2, 4, 6, 8, and 10 by the addition of 0.1M HCl or NaOH solution and carried out at 35°C. Three different temperatures (30, 40 and 60 °C) were conducted by fixing the pH at 1.27. The kinetics experiments were carried out at an initial concentration 100 mg L⁻¹, temperature of 35 °C, pH 1.27. The adsorption procedures concerning pH, temperature and kinetic study were similar to that determining the adsorption isotherm.

3. Result and Discussion

3.1 Adsorption Isotherm of Cd^{2+}

The adsorption isotherm data were commonly analyzed on the basis of Langmuir [8] and Freundlich [9] models. Langmuir isotherm is based on the assumption that adsorption takes place on a homogeneous adsorbent surface of identical sites which are equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbate molecules. If the Cd^{2+} adsorption follows the Langmuir model, the adsorption process can be expressed as:

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

where c_e (mg/L) is the equilibrium concentration of Cd^{2+} in solution, q_e (mg/g) the adsorption capacity at equilibrium, q_m (mg/g) the maximum adsorption capacity and K_L is the effective dissociation constant. The Langmuir equation obeys Henry's Law at low concentrations.

The Freundlich [9] equation is assumed that the adsorption surface sites have different Cd^{2+} binding energies. The Freundlich isotherm model is usually adopted for heterogeneous adsorption [10]. If the Cd^{2+} adsorption follows the Freundlich model, the adsorption process can be expressed as:

$$q_e = K_F (c_e)^{1/n} \quad (2)$$

where q_e ($mg L^{-1}$) is the adsorption capacity at equilibrium, c_e ($mg L^{-1}$) is the equilibrium concentration of Cd^{2+} in solution, and K_F and n are the physical constants of the Freundlich adsorption isotherm. Experimental values of n are usually greater than unity and this means that the forces between the adsorbed molecules are repulsive. However, the values of n are closer to zero means the system is more heterogeneous [10].

The experimental results have demonstrated that the equilibrium data or the relationship between adsorbing capacity (q_e) and equilibrium mass concentration (c_e) are fitted well by Freundlich isotherm equation, indicating that heterogeneous adsorption occurs (Fig. 1). The Langmuir and Freundlich constant and the coefficient of multiple determination (R^2) between the experimental values and the predicted value using the models are given in Table 2. According to the R^2 value of Freundlich model are closer to 1 than another one, this confirms that the Freundlich isotherm is better fitted.

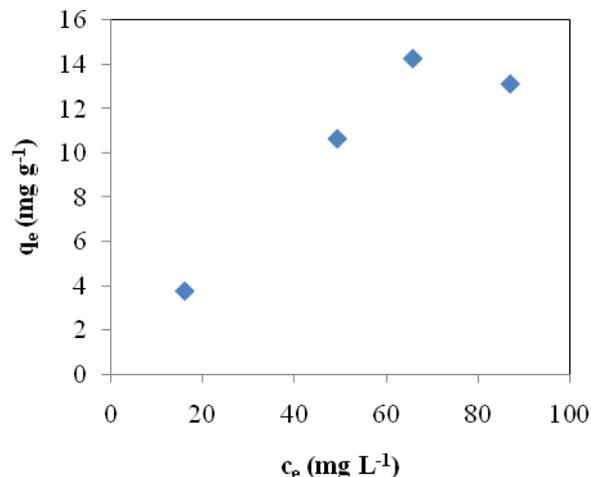


Figure 1 Adsorption Isotherm of cadmium on montmorillonite clay (pH 1.27; temperature 35°C; amount of montmorillonite 0.20g).

Table 2 Comparison of the adsorption isotherm coefficients and R^2 value between experimental and predicted values by Langmuir and Freundlich models.

Langmuir model			Freundlich model		
K_L	q_m	R^2	K_F	n	R^2
0.287	0.008	0.644	0.407	1.23	0.948

3.2 Influence of solution pH on Cd^{2+} adsorption

The amount of adsorption of metal ions on clay increases with increasing solution pH (Fig. 2). At low pH the metal adsorption is low which can be explained by the competitive adsorption between proton and metal ions. As the solution pH increases, the number of negatively charged sites increases because the silanol groups on the surface become increasingly deprotonated. It causes the increase of number of negatively charged sites and thus the metal cations adsorption on clay surface increases. The variation of amount of H^+ and OH^- in the solution can be cause of the protonate and deprotonate of the surface functional groups on clay mineral by adsorption of H^+ or OH^- ions. In addition, Cd^{2+} can be precipitated with OH^- ions or pH value is above 6.0. Thus, at pH above 6.0 there are two mechanisms to remove Cd^{2+} from the aqueous solution, which are ion exchange and precipitation. It is concluded that precipitation occurs in general at higher pH while ion exchange predominates at lower pH solution [11].

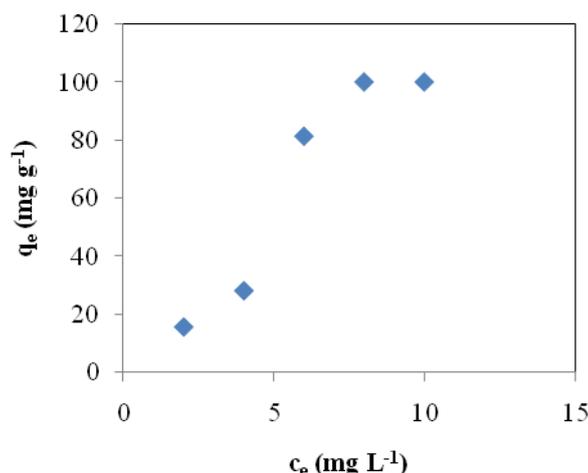


Figure 2 Effect of initial solution pH on sorption of Cd^{2+} (initial solute concentration of Cd^{2+} , 100 mg/L; temperature 35°C; amount of montmorillonite 0.20g).

3.3 Thermodynamic studies

The amount of Cd^{2+} adsorbed slight decreases from 7.94 to 6.97 mg g⁻¹ (12% decrease) when the temperature was raised from 40 to 60 °C (Fig. 3). The decrease is not usually observed. The thermodynamic parameters are important for a better understanding of the effect of temperature on adsorption. The equilibrium partition constant K_d is calculated as follows

$$K_d = \frac{q_e}{c_e} \quad (3)$$

The following relationships have been used to evaluate the thermodynamic parameters ΔG° , ΔH° , and ΔS° [12, 13].

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$\log_{10} K_d = \left(\frac{\Delta H^\circ}{2.303R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad (5)$$

where R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). According to Eq. (3), the unit of q_e that are used for calculation is mg kg^{-1} and the unit of c_e is mg L^{-1} . The change in free energy (ΔG°) is calculated to be -11.57, -11.75 and -12.11 kJ/mol (at 40, 50, and 60°C, respectively) from eq. (4). The ΔG° is negative value which means that the sorption of metal ion on clay is spontaneous. As clearly shown in Eq. (5), a plot of $\log K_d$ versus $1/T$ would give ΔH° and ΔS° (Fig. 4). The values of ΔH° and ΔS° are $+3.1 \text{ J mol}^{-1}$ and $+26.96 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

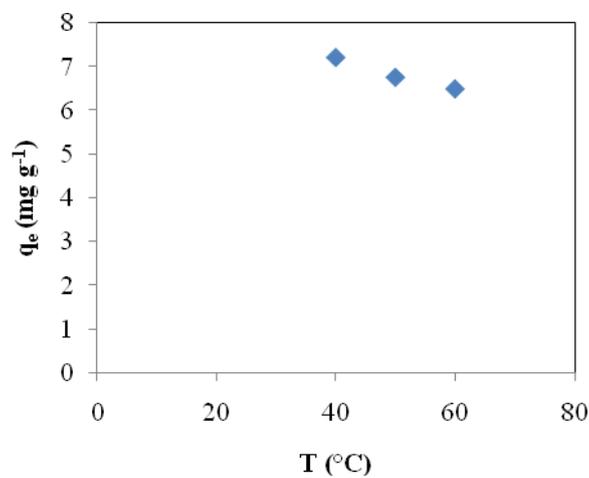


Figure 3 Effect of temperature on sorption of Cd^{2+} (initial solute concentration of Cd^{2+} , 100 mg/L; temperature 35°C: amount of montmorillonite 0.20g, pH 1.27).

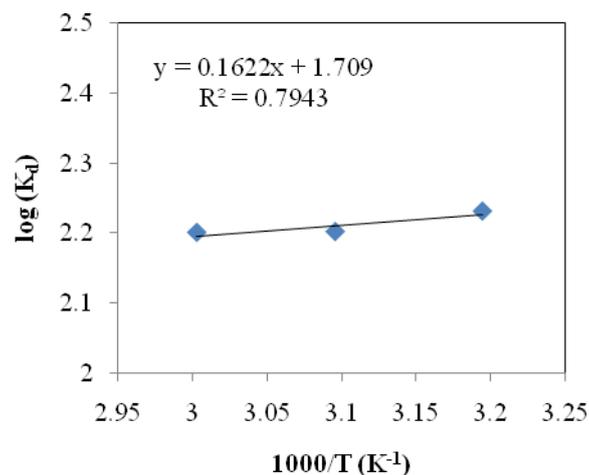


Figure 4 Determination of thermodynamic parameters for sorption of Cd^{2+} using the montmorillonite clay.

3.4 Adsorption kinetic of Cd²⁺

The sorption of Cd²⁺ on the clay was rapid and the equilibrium was attained within 15 min (Fig. 5). The amount of Cd²⁺ adsorbed (q_t) rapid increases from 0 to 15 mg g⁻¹ when the time rises to 15 min.

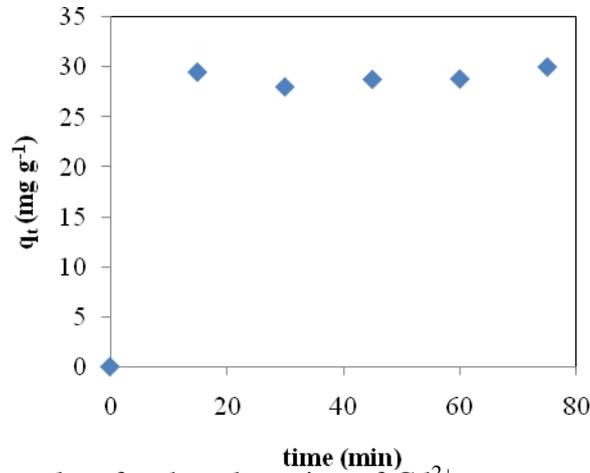


Fig 5 Adsorption kinetics plots for the adsorption of Cd²⁺ onto montmorillonite clay (initial solute concentration of Cd²⁺, 100 mg/L; temperature 35°C; amount of montmorillonite 0.20g, pH 1.27).

The experimental data were fitted by applying pseudo-first-order (Eq. (6) [14]), pseudo-second-order (Eq. 7 [14]), and intraparticle diffusion (Eq. 8 [14]) models in order to gain a better understanding of the adsorption process.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = k_3 t^{1/2} \quad (8)$$

In the above equations, q_e (mg L⁻¹) and q_t (mg L⁻¹) are the amounts of Cd²⁺ adsorbed at equilibrium and at any contact time of adsorption t (h), respectively; k_1 (h⁻¹), k_2 (g mg⁻¹ h⁻¹), and k_3 (mg g⁻¹ h^{-1/2}) are the pseudo-first-order, pseudo-second-order, and intraparticle diffusion rate constant, respectively.

According to Eq. (6), the plot of $\ln(q_e - q_t)$ versus t , and according to Eq. (8), the plot of q_t versus $t^{1/2}$ did not provide a straight line for the respective model. It shows that poor correlation coefficient values. Accordingly, the experimental data do not conform to either of these models.

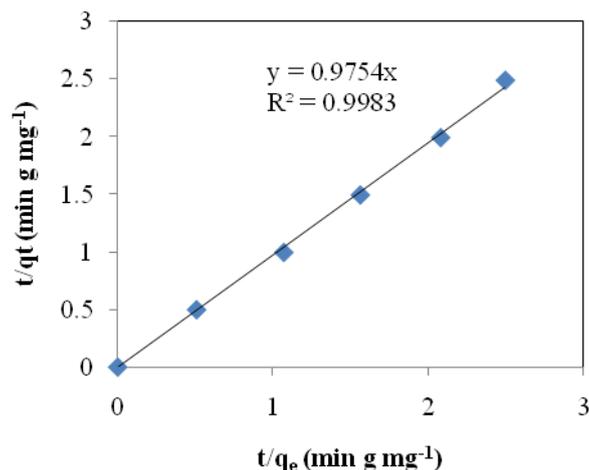


Fig 6 Pseudo-second-order plots for the adsorption of Cd^{2+} onto montmorillonite clay at various temperatures (initial solute concentration of Cd^{2+} , 100 mg/L; amount of montmorillonite 0.20g, pH 1.27).

According to Eq. (8), the plot of t/q_t against t provides the straight line curve, as is shown in fact to be the case. The high value of R^2 (0.9983) for temperature as 35°C indicates that the adsorption data confirm well to pseudo-second-order kinetics for the entire adsorption process.

Conclusion

In the present study, the removal of Cd^{2+} from aqueous solution was investigated by using montmorillonite as an adsorbent, a natural clay mineral. This material has been demonstrated to be highly effective for the removal of Cd^{2+} from aqueous solution. The adsorption equilibrium was attained within times of less than 15 min. The best-fit adsorption isotherm was achieved with the Freundlich and not the Langmuir model, indicating that heterogenous adsorption occurs. The enthalpy change for the adsorption process ($+3.1\text{J mol}^{-1}$) confirms the endothermic nature of adsorption, while a free energy change falling in the range -11.57 to -12.11kJ mol^{-1} confirms the spontaneous process. Adsorption is therefore dependent on a substantial positive entropy change consistent with increased randomness at the solid/solution interface. The adsorption of Cd^{2+} onto montmorillonite obeyed pseudo-second-order kinetics.

References

- [1] Matlock, M., M., Howerton, B., S., Henke, K., R., Atwood, D., A. (2001). Apyridine-thiol ligand with multiple bonding sites for heavy metal precipitation, *J. Hazard. Mater.* 82: 55 - 63.
- [2] Lee, I., H., Kuan, Y., C., Chern, J., M. (2009). Fractional experimental design for recovering heavy metal from sludge with ion-exchange resin, *J. Colloid Interface Sci.* 333: 46-53.
- [3] Fan, H.T., Aderson, P.R. (2005). Copper and cadmium removal by Mn oxide-coated granular activated carbon, *Sep. Purifi. Technol.* 45: 61-67.
- [4] Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E. (2003). Adsorption of heavy metals on Na-Montmorillonite. Effect of pH and organic substances, *water research* 37: 1619-1627.

- [5] Zhu, L., Ren, X., Yu, S. (1998). Use of cetyltrimethylammonium bromide-bentonite to remove organic contaminants of varying polar character from water, *Environ. Sci. Technol.* 32: 3374.
- [6] Schindler, P.W., Fürst, B., Dick, R., Wolf, P.U. (1976). Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+} , Cu^{2+} , Cd^{2+} and Pb^{2+} . *J. Colloid Interface Sci.* 55(2): 469 -475.
- [7] Mercier, L. and Detellier, C. (1995). Preparation, characterization, and applications as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite. *Environ. Sci. Technol.* 29(5):1318-1323.
- [8] Freundlich, H. (1907). An adsorption in solutions, *Zeitschrift für Physikalische Chemie* 57: 385-471.
- [9] Yilmaz, M. Bayramoglu, G., Arica, M.Y., Separation and purification of lysozyme by reactive green 19 immobilised membrane affinity chromatography, *Food Chem.* 89: 11-18.
- [10] Asci, Y. Nurbas, M. Sag Acikel. (2008). A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant, *J. Hazard. Mater.* 154: 603-673.
- [11] Bradl, H.B. (2004). Adsorption of heavy metal ions on soils and soils constituents, *J. Colloid Interface Sci.* 277: 130-139.
- [12] Zhu, L, Ren., X., Yu, S., Use of cetyltrimethylammonium bromide-bentonite to remove organic contaminants of varying polar character from water, *Environ. Sci. Technol.* 32: 3374.
- [13] Hasany, S.M., Chaudhry, M.H. (1998). Fixation of Cr(III) traces onto Haro river sand from acidic solution, *J. Radiational. Nucl. Chem.* 230:11.
- [14] Almeida, C.A.P., Debacher N.A., Downs, A.J., Cottet, L., and Mello, C.A.D. (2009). Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J. Colloid Interface Sci.* 332: 49-53.