

# Adsorption Characteristics of Leonardite for Removal of Cd(II) and Zn(II) from Aqueous Solutions

Apiradee Terdputtakun, Orn-Anong Arqueropanyo, Sorapong Janhom, Ponlayuth Sooksamiti, and Wimol Naksata

**Abstract**—Leonardite was used as an adsorbent for the removal of Cd(II) and Zn(II) from aqueous solutions. The characteristics of leonardite were determined using XRD, XRF, FTIR, and SEM. Adsorption of Cd(II) and Zn(II) on leonardite, in batch system at 30 °C, was investigated to achieve the optimum condition for metals removal. Studies were carried out at different pH, contact time, and initial metal concentration. It was found that adsorption of metals ions was strongly influenced by pH value. The optimum adsorption conditions obtained were pH 6 and contact time of 60 min. Adsorption data were interpreted to kinetic models, including pseudo-first-order, pseudo-second-order, intra-particle diffusion, and adsorption isotherm models, including Langmuir isotherm and Freundlich isotherm. Pseudo-second-order kinetic model was suitable for describing adsorption of Cd(II) and Zn(II) on leonardite. Both Langmuir and Freundlich isotherms fitted well with the adsorption data of Zn(II) whereas the adsorption of Cd(II) better fitted to Freundlich isotherm.

**Index Terms**—Leonardite, adsorption, kinetic, isotherm.

## I. INTRODUCTION

Rapid growth of manufacturing industries is resulting in environmental problems. One of the main reasons behind the problems is the production and utilization of heavy metals in the industrial activities such as metal smelting and refining, pigments, electroplating, metallurgical alloying, battery manufacturing, fertilizers, and chemical industries. Some metals are highly toxic even at low concentration i.e. lead, cadmium, arsenic, and mercury.

Cadmium and zinc are among the metals that generally used in the industries. Cadmium also occurs naturally in ores together with zinc. Cadmium is classified as human carcinogen. Long-term high cadmium exposure may cause kidney and skeletal damage (itai-itai disease) [1]. Compared to cadmium, zinc has low human toxicity. Although zinc is an essential element required in human body, but excess exposure of zinc can be harmful, and causes zinc toxicity.

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In the industrial processes, leakage of metals can be occurred in several pathways. Metals may contaminate in water and release to the environment along with the wastewater. These can be harmful to aquatic life, animals and human. Most of metals ions can dissolve in water and accumulate in environment. Furthermore, they cannot be eliminated by natural processes. Metals can enter the body and produce adverse biological effects on survival, activity, growth, metabolism, and reproduction of organisms [2]. Exposure of metals leads to acute and/or chronic diseases in human. Therefore, the treatment of wastewater before releasing to water sources is required.

Various techniques have been applied for the removal of metals from wastewater including precipitation, adsorption, electrochemical treatment, photocatalysis, ion exchange, and membrane filtration [3], [4]. Several techniques are expensive and complicate for large scale applications. Adsorption is considered as an effective process for metal removal. This technique is simple, economical, flexible, and sludge-free. Different kinds of adsorbents are used for wastewater treatment such as activated carbon, zeolite, clay, algae, and peat. The removal efficiency of adsorbents depends on the characteristics of adsorbents. The properties of adsorbent should be high capacity, cheap, easily available, selectivity and can be regenerated. Recently, attention has been focused on the utilization of natural materials, which are the waste from agricultures and industries as adsorbent. These materials are available in large quantity and the cost is relatively low. The adsorption efficiency of natural materials such as rice husk, peat, tea-industrial waste, fly ash, bottom ash, cellulose, and banana peel had been investigated for the removal of metal from aqueous solutions [5], [6].

Leonardite is an oxidized product of lignite. It possesses low fuel ratios and heating values, which make it unsuitable as fuels. Leonardite can be used as soil-conditioner, bio-catalyst and bio-stimulant for plants, and drilling additive. It contains large amounts of humic substances (humic acids and fulvic acids). Humic materials are complex organic molecules that contain various functional groups such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O). These functional groups have the ability of binding with metal cations through the electrostatic attraction [7].

Mae Moh mine, located in the northern of Thailand, produces a huge amount of leonardite which is the byproduct of mining. Large deposits of leonardite were left on the site. Thus, it is interesting to use leonardite as adsorbent for removal of metals. The understanding of characteristics, adsorption capacity and affinity of leonardite is an important thing for efficient application. In this work, the adsorption ability of leonardite for the individual removal of Cd(II) and

Zn(II) ions from aqueous solutions was evaluated. The effect of important factors such as pH, contact time, and metal concentration on the adsorption capacity were also studied. The kinetic and equilibrium constants of adsorption were established and modeled.

## II. MATERIALS AND CHEMICALS

Leonardite obtained from Mae Moh lignite mine (Lampang, Thailand), was chosen as adsorbent. It was air dried, powdered, and size adjusted by sieving through a 80 mesh screen before being used. Characterization of leonardite was investigated by several techniques. The analysis of chemical and mineralogical compositions of leonardite was made by using X-ray fluorescence (XRF) (Phillips, Magix pro sequential) and X-ray diffraction (XRD) (Bruker, D2 Phaser), respectively. The Fourier transform infrared (FTIR) spectrum was also recorded in the range of wavenumber 4000 – 400  $\text{cm}^{-1}$  on a Bruker Tensor 27 spectrometer. Morphology of leonardite was studied using scanning electron microscope (Joel, model JSM-5910). Specific surface area was determined by nitrogen adsorption (BET) at 77 K using Autosorb 1 MP, Quantachrome.

All chemicals used throughout this study were of analytical reagent grade.  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (Himedia, India) and  $\text{ZnCl}_2$  (Rankem, India) were dissolved in deionized water as stock solutions (500  $\text{mg L}^{-1}$ ), and were further diluted to the desired concentrations. The pH adjustment was made by using 1 M NaOH and 1 M HCl solutions.

## III. ADSORPTION EXPERIMENTS

Batch process was carried out to study the adsorption behavior of Cd(II) and Zn(II) on leonardite. The parameters that affect the adsorption process including pH, contact time and initial metal concentration were investigated. Effect of pH value on the adsorption of Cd(II) and Zn(II) was studied at different pH values between 2–6. In the experiments, 0.1 g of leonardite was added to each 100 mL metal solution whose pH had been previously adjusted to the desired values. After the addition of adsorbent, pH was re-adjusted. Erlenmeyer flasks containing the mixture were then agitated continuously at speed of 120 rpm, 30 °C in thermostatic water-bath shaker for 5 h. After the agitation, metal solutions were separated from leonardite by filtration and were taken to determine the remaining metal concentration using atomic absorption spectrophotometer (Perkin Elmer, model 3110). The metal ion adsorbed amount at equilibrium,  $q_e$  ( $\text{mg g}^{-1}$ ) was calculated as follow:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium metal concentrations ( $\text{mg L}^{-1}$ ), respectively.  $V$  is the volume of metal solution (L) and  $W$  is the weight of leonardite (g).

To study Cd(II) and Zn(II) adsorption kinetics, the experiments were performed at optimum pH (as determined from pH experiments) with a total time of 5 h. The initial

metal concentration of Cd(II) and Zn(II) for kinetic studies was 30  $\text{mg L}^{-1}$ . Aliquots were taken at suitable time intervals. Each aliquot was filtered and determined the remaining metal concentration. Adsorption isotherms were investigated under the conditions of optimum pH and contact time. The initial metal concentration range studied was 5–50  $\text{mg L}^{-1}$ .

## IV. RESULTS AND DISCUSSIONS

### A. Characterization of Leonardite

The chemical and mineralogical compositions of leonardite are given in Table I. It shows the presence of alumina, silica, and ferric oxide as major inorganic component whereas other oxides are presented in trace amount. The loss on ignition indicates that leonardite contains less than 37% organic matter. Mineralogical compositions of leonardite, observed by XRD analysis are quartz, illite, and muscovite.

TABLE I: COMPOSITION OF LEONARDITE

Chemical Composition	% wt	Mineralogical Composition
$\text{Al}_2\text{O}_3$	16.280	Quartz
$\text{SiO}_2$	28.949	Illite
$\text{MgO}$	0.838	Muscovite
$\text{P}_2\text{O}_5$	0.680	
$\text{K}_2\text{O}$	2.287	
$\text{CaO}$	2.826	
$\text{TiO}_2$	0.728	
$\text{Fe}_2\text{O}_3$	10.371	
$\text{Rb}_2\text{O}$	0.072	
$\text{SrO}$	0.113	
$\text{ZrO}_2$	0.086	
LOI	36.80	

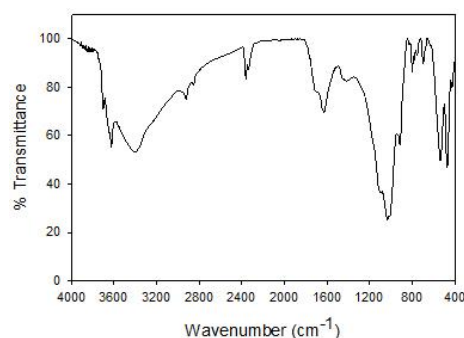


Fig. 1. FTIR spectrum of leonardite.

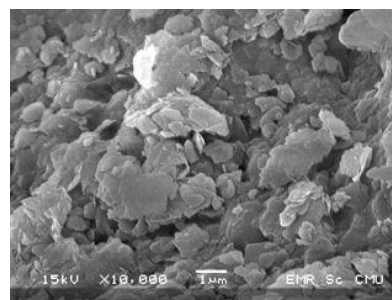


Fig. 2. SEM image of leonardite.

The FTIR spectrum of leonardite is shown in Fig. 1. The stretching vibration of the Si–O groups at 1033, 799, and 780  $\text{cm}^{-1}$  with the bending vibration of Si–O groups at 697, 535, and 471  $\text{cm}^{-1}$  are assigned to quartz [8], [9]. The stretching

vibration of OH-groups at  $3623\text{ cm}^{-1}$ , the Al-OH-Mg deformation at  $827\text{ cm}^{-1}$ , the Al-O-Si vibration at  $754\text{ cm}^{-1}$  and Al-OH-Al deformation at  $914\text{ cm}^{-1}$  indicates illite [9], [10]. It was considerably difficult to identify the difference between illite and muscovite because both minerals exhibited similar absorption bands [10]. The FTIR spectrum of leonardite also reveals the bands of organic matter "humic substances". The broad band between  $3600 - 3200\text{ cm}^{-1}$  is assigned to the O-H/N-H stretching vibration of phenols, amines/amides, and carboxylic acids. The double bands at  $2922$  and  $2852\text{ cm}^{-1}$  attributes to C-H stretching vibration of alkanes. The stretching vibration band of C=O groups of carboxylic acids and ketones is observed around  $1698\text{ cm}^{-1}$ . The presence of absorption band at  $1629\text{ cm}^{-1}$  is due to stretching vibration of C=C bonds in aromatic rings and possibly to the stretching vibration of C=O of conjugated ketones and carboxylic groups. The absorption band at  $1419\text{ cm}^{-1}$  is assigned to C-H bending vibration of alkanes.

On the SEM image of leonardite (Fig. 2), the corn flake-like morphology was observed. Leonardite has a BET ( $\text{N}_2$ ) specific surface area of  $19.67\text{ m}^2\text{ g}^{-1}$ .

### B. Effect of PH

The pH value is one of the important factors in the adsorption process. It affects on the degree of ionization of metal ion species and surface charge of adsorbent, all of that can lead to the different adsorption behavior and capacity. In the pH range studied, Cd(II) and Zn(II) were found as free ions, no precipitation occurred [11], [12]. Fig. 3 demonstrates the adsorption of Cd(II) and Zn(II) onto leonardite from aqueous solution with initial metal concentration of  $30\text{ mg L}^{-1}$  at pH 2-6. Adsorption of both metals was found to be strongly dependent on pH values. In strong acidic condition, adsorbed amounts were relatively low. This can be described by the protonation of functional groups found in leonardite. The dissociation of functional groups can be controlled by solution pH. Carboxyl groups start to dissociate the protons at slightly acidic up to neutral region [13]. Silanol groups dissociate at above pH 4 [14]. Thus, at low pH values, mostly of functional groups are protonated. Less active site is available for adsorption of metal ions leading to poor adsorption. Phenolic groups were not expected to cooperate with metal ions in the pH range studied because the dissociation starts at pH 9.

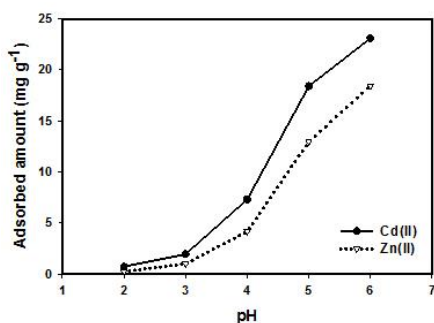


Fig. 3. Effect of pH on Cd(II) and Zn(II) adsorption for leonardite. (Cd(II)  $30\text{ mg/L}$ , Zn(II)  $30\text{ mg/L}$ ,  $30\text{ }^\circ\text{C}$ , 5 hr).

As the pH increases, more dissociation takes place and the negatively charged sites increase. Metal ions can be more

adsorbed with the increasing pH. The maximum adsorbed amount of Cd(II) and Zn(II) were observed at pH 6. From the results, pH 6 was the suitable pH for adsorption of Cd(II) and Zn(II) on leonardite and was applied in further experiments.

### C. Kinetic Studies

The relationship between contact time and metal ions uptake by leonardite is shown in Fig. 4. It was found that Cd(II) and Zn(II) rapidly adsorbed on leonardite at initial contact time. After 10 min, adsorption processes proceeded slowly. No significant change was observed after 60 min. Hence, the contact time of 60 min was considered as equilibrium time for adsorption of Cd(II) and Zn(II) onto leonardite and was used in all adsorption experiments.

In order to describe the kinetic of Cd(II) and Zn(II) adsorption processes, the experimental data were analyzed by pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.

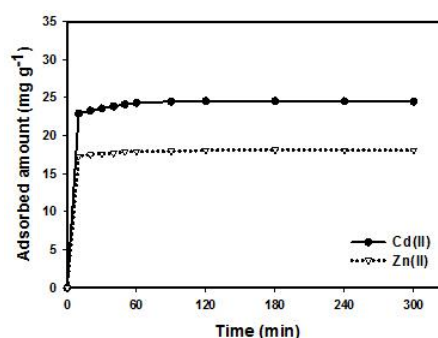


Fig. 4. Effect of contact time on Cd(II) and Zn(II) adsorption for leonardite (Cd(II)  $30\text{ mg/L}$ , Zn(II)  $30\text{ mg/L}$ ,  $30\text{ }^\circ\text{C}$ , pH 6).

#### 1) Pseudo-first-order model

Pseudo-first-order kinetic equation was suggested by Lagergren in 1898 [15]. It has been used in liquid-solid adsorption systems. It is based on the adsorption capacity. The equation can be expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the adsorbed amount at time "t" and at equilibrium, respectively.  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo first-order adsorption.

Equation (2) was integrated with the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  and rearranged in linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

If the plot of  $\log(q_e - q_t)$  versus  $t$  lies on the straight line, the adsorption system will follow the pseudo-first-order kinetic. The pseudo-first-order rate constant,  $k_1$  and equilibrium adsorbed amount,  $q_e$  can be calculated from slope and intercept, respectively.

Fig. 5 shows the plot of pseudo-first-order kinetic for the adsorption of Cd(II) and Zn(II) on leonardite for the initial 60 min. It can be observed that the plots of Cd(II) and Zn(II) deviated from the straight line. The values of  $k_1$ ,  $q_e$  and correlation coefficient ( $R^2$ ) are presented in Table II. The

correlation coefficient of Cd(II) and Zn(II) were 0.931 and 0.919, respectively. These values were considerably high but the calculated  $q_e$  values for both metals were much lower than experimental  $q_e$  values. The calculated  $q_e$  values of Cd(II) and Zn(II) were 2.88 and 1.46 mg g<sup>-1</sup>, respectively whereas the  $q_e$  values of Cd(II) and Zn(II) obtained from the experiments were 24.5 and 18.0 mg g<sup>-1</sup>. This indicates that pseudo-first order model is not applicable for adsorption of Cd(II) and Zn(II) on leonardite.

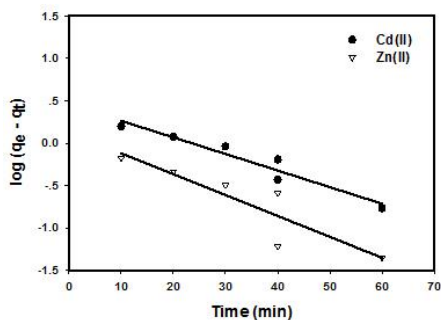


Fig. 5. Pseudo-first-order kinetic plot for the adsorption of Cd(II) and Zn(II) on leonardite.

TABLE II: KINETIC PARAMETERS FOR CADMIUM AND ZINC ADSORPTION ONTO LEONARDITE

Kinetic model	Cd(II)	Zn(II)
$q_e, \text{exp (mg g}^{-1}\text{)}$	24.5	18.0
Pseudo-first-order		
$q_e, \text{cal (mg g}^{-1}\text{)}$	2.88	1.46
$k_1 \text{ (min}^{-1}\text{)}$	0.0451	0.0567
$R^2$	0.931	0.919
Pseudo-second-order		
$q_e, \text{cal (mg g}^{-1}\text{)}$	24.6	18.1
$k_2 \text{ (g mg}^{-1} \text{min}^{-1}\text{)}$	0.0377	0.0897
$R^2$	1.00	1.00
Intra-particle diffusion		
$k_{id} \text{ (mg g}^{-1} \text{min}^{-0.5}\text{)}$	0.102	0.051
$C \text{ (mg g}^{-1}\text{)}$	23.1	17.4
$R^2$	0.677	0.751

### 2) Pseudo-second-order model

Pseudo-second-order kinetic has been widely applied in many adsorption systems. The pseudo-second order equation can be represented in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of pseudo-second order adsorption. After integration of equation (4) with the same boundary conditions as above and rearranged the equation, it gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The pseudo-second-order rate constant,  $k_2$  and equilibrium adsorbed amount,  $q_e$  can be determined from slope and intercept of plot of the  $t/q_t$  against  $t$ .

The pseudo-second order kinetic plots for the adsorption

of Cd(II) and Zn(II) by leonardite (Fig. 6) show a straight-line pattern results. Parameters and correlation coefficient of pseudo-second order kinetic were listed in Table II. The correlation coefficients for both metals were 1.00 and the calculated  $q_e$  values were very close to the experimental  $q_e$  values. The high correlation coefficients and the good agreement between calculated and experimental  $q_e$  suggest that the adsorption of Cd(II) and Zn(II) on leonardite follow the pseudo-second order model. The pseudo-second order model is based on the assumption that the adsorbate was adsorbed onto two surface sites [16].

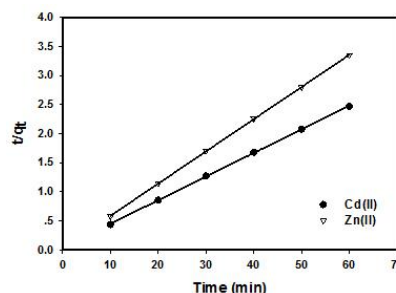


Fig. 6. Pseudo-second-order kinetic plot for the adsorption of Cd(II) and Zn(II) on leonardite.

### 3) Intra-particle diffusion model

Intra-particle diffusion model was developed by Webber and Morris [17]. This model was used for predicting the adsorption mechanisms. The intra-particle diffusion model is expressed as:

$$q_t = k_{id}t^{0.5} + C \quad (6)$$

where  $k_{id}$  (mg g<sup>-1</sup> min<sup>-0.5</sup>) is intra-particle diffusion rate constant, and  $C$  (mg g<sup>-1</sup>) is the constant related to the thickness of boundary layer.

If plot of  $q_t$  versus  $t^{0.5}$  gives a straight line passing through the origin, then the adsorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process. The slope of the plot gives the value of  $k_{id}$ , and intercept gives the value of  $C$ .

Fig. 7 presents the plots of Cd(II) and Zn(II) uptake against  $t^{0.5}$ . Plots of Cd(II) and Zn(II) deviate from the origin and exhibit two types of linearity indicating two diffusion process. It can be suggested that the adsorption of Cd(II) and Zn(II) might be controlled by both film and intra-particle diffusions. The intra-particle diffusion parameters are shown in Table II.

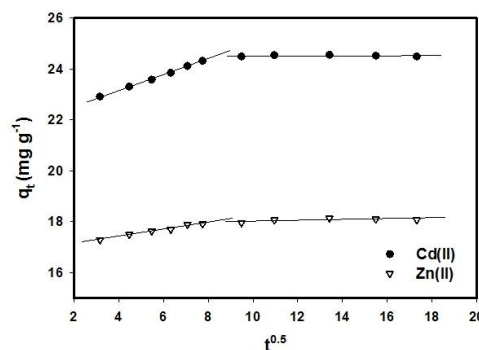


Fig. 7. Intra-particle diffusion plot for the adsorption of Cd(II) and Zn(II) on leonardite.



D. Adsorption Isotherms

Generally, adsorption isotherm is used to describe the relation between the amount of adsorbate adsorbed by adsorbent and amount of adsorbate remaining in the medium at equilibrium and constant temperature. It can provide the information about adsorption capacity and affinity between adsorbate and adsorbent. In the present study, the experimental equilibrium data were tested to Langmuir and Freundlich isotherms.

E. Langmuir Isotherm

Langmuir isotherm assumes that the adsorption takes place on the homogeneous surface, no interaction between adsorbed molecules and all the adsorption occurs through the same mechanism until a monolayer of adsorbate is obtained. The Langmuir isotherm equation is expressed by the following empirical equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{6}$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity of adsorbent and  $b$  ( $\text{L mg}^{-1}$ ) is Langmuir constant related to adsorption intensity. This equation can be linearized as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{7}$$

From the plot of  $C_e/q_e$  against  $C_e$ , the values of  $q_m$  and  $b$  can be determined from the slope and intercept.

F. Freundlich Isotherm

Freundlich isotherm is based on the adsorption on heterogeneous surface where the adsorption energy is not equivalent for adsorption sites, and therefore the adsorption is not limited to monolayer. Multi-layer adsorption can occur on the adsorption sites. The Freundlich isotherm equation is given:

$$q_e = K_F C_e^{1/n} \tag{8}$$

The linear form of Freundlich isotherm equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

where  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and heterogeneity. The values of  $n$  and  $K_F$  can be calculated from slope and intercept of the plot  $\log q_e$  against  $\log C_e$ .

Adsorption isotherms of Cd(II) and Zn(II) are presented in Figs. 8 and 9, respectively. It was found that the adsorbed amount increases with increasing the initial metal concentration. The Langmuir and Freundlich isotherm parameters, together with the correlation coefficients, were listed in Table III. As can be seen, the correlation coefficient of Freundlich isotherm was higher than that of Langmuir isotherm for Cd(II). It indicates that the adsorption of Cd(II)

on leonardite follows Freundlich isotherm.

TABLE III: LANGMUIR AND FREUNDLICH ISOTHERMS PARAMETERS FOR CADMIUM AND ZINC ADSORPTION ON LEONARDITE

Metal	Langmuir isotherm			Freundlich isotherm		
	$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$	$n$	$R^2$
Cd(II)	37.0	0.496	0.968	13.1	2.91	0.994
Zn(II)	21.5	0.337	0.992	7.07	3.06	0.990

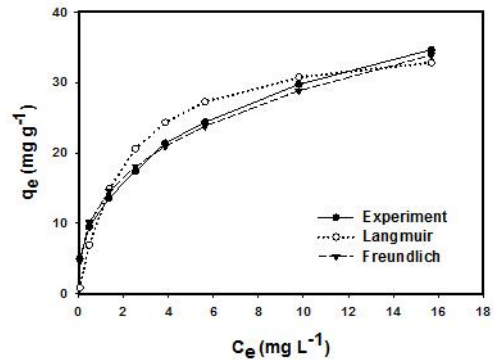


Fig. 8. Adsorption isotherm of Cd(II) on leonardite.

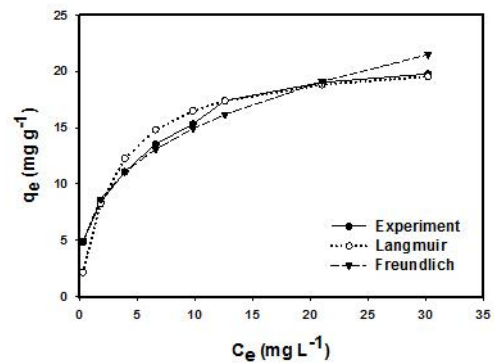


Fig. 9. Adsorption isotherm of Zn(II) on leonardite

According to the assumption of Freundlich isotherm, it can be suggested that adsorption of Cd(II) might be multilayer and also predicted the heterogeneity of the adsorbent surface. The high magnitude of  $K_F$  shows the high uptake of Cd(II). Since the  $n$  value was found to be greater than 1, it was classified as favorable adsorption.

For Zn(II), the correlation coefficient for Langmuir and Freundlich isotherm were 0.992 and 0.990, respectively. Both isotherms were able to describe the adsorption of Zn(II). The maximum adsorption capacity calculated from Langmuir equation was  $21.5 \text{ mg g}^{-1}$  and the adsorption is favorable ( $n > 1$ ).

V. CONCLUSION

The characteristics of leonardite and the adsorption behavior for removal of Cd(II) and Zn(II) from aqueous solution were studied. The results of characterization revealed that leonardite composed of mineral and organic matters which bear the variety of functional groups. These functional groups play an important role on the adsorption process. For adsorption studies, pH value, contact time, and initial metal concentration were found to have the effects on the adsorption efficiency. Adsorbed amount was small at low pH. Cd(II) and Zn(II) were best adsorbed at pH 6. The

adsorption of metal ions on leonardite was fast and reached the equilibrium within 60 min. Pseudo-second-order can be used to describe the kinetic adsorption of Cd(II) and Zn(II). The intra-particle diffusion was not the only rate-controlling step for adsorption of metals ions. Adsorption mechanisms of both metals were controlled by film and intra-particle diffusions. Adsorption of Cd(II) was found to be fitted to Freundlich isotherm whereas the adsorption of Zn(II) was agree well with both Langmuir and Freundlich isotherms. The maximum adsorbed amount of Cd(II) and Zn(II) were 37.0 and 21.5 mg g<sup>-1</sup>, respectively. Leonardite is a low-cost material which has a good efficiency for metal ions adsorption. It can be an alternative adsorbent for the treatment of metal-contaminated water.

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#### REFERENCES

[1] L. Jarup, "Hazards of heavy metal contamination," *Br. Med. Bull.*, vol. 68, pp. 167-182, 2003.

[2] F. Solomon. (2008). Impacts of metals on aquatic ecosystems and human health. *Environment and communities*. [Online]. pp. 14-19. Available: <http://www.infomine.com/library/publications/docs/Mining.com/Apr2008c.pdf>

[3] M. A. Baraket, "New trends in removing heavy metals from industrial wastewater," *Arab. J. Chem.*, vol. 4, pp. 361-377, 2011.

[4] F. Fu and Q. Wang, "Removal of heavy metal ions from wastewater: A review," *J. Environ. Manage.*, vol. 92, pp. 407-418, 2011.

[5] S. K. Yadnanparthi, D. Graybill, and R. V. Wandruszka, "Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters," *J. Hazard. Mater.*, vol. 171, pp. 1-15, 2009.

[6] S. N. Abas, M. Ismail, M. L. Kamal, and S. Izhar, "Adsorption process of heavy metals by low cost adsorbent: A review," *World. Appl. Sci. J.*, vol. 11, pp. 1518-1530, 2013.

[7] E. Tipping, *Cation Binding by Humic Substances*, Cambridge, U.K.: Cambridge University Press, 2004, ch. 8, pp. 157-161

[8] B. J. Saikia, G. Parthasarathy, and N. C. Sarmah, "Fourier transform infrared spectroscopic estimation of crystallinity in SiO<sub>2</sub> based rocks," *Bull. Mater. Sci.*, vol. 31, pp. 775-779, 2008.

[9] P. S. Nayak and B. K. Singh, "Instrumental characterization of clay by XRF, XRD and FTIR," *Bull. Mater. Sci.*, vol. 30, pp. 235-238, 2007.

[10] L. Vaculikova and E. Plevova, "Identification of clay minerals and micas in sedimentary rocks," *Acta Geodyn. Geomater.*, vol. 2, pp. 167-175, 2005.

[11] H. Babich and G. Stotzky, "Effects of cadmium on the biota: Influence of environment factors," *Advances in applied microbiology*, vol. 23, New York: Academic Press, 1978, pp. 60-62.

[12] L. K. Wang, J. P. Chen, Y. T. Huang, and N. K. Shammas, *Heavy Metals in the Environment*, U.K.: CRC Press, 2009, ch. 6, pp. 181-186.

[13] M. Havelcova, J. Mizera, I. Sykorova, and M. Pekar, "Sorption of metal ions on lignite and the derived humic substances," *J. Hazard. Mater.*, vol. 161, pp. 559-564, 2009.

[14] S. C. Moldoveanu and V. David, *Modern Sample Preparation for Chromatography*, U.K.: Elsevier, 2015, ch. 7, p. 234.

[15] D. Mohan, C. U. Pittman, and P. H. Steele, "Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on kraft lignin- a biosorbent," *J. Colloid Interface Sci.*, vol. 297, pp. 489-504, 2006.

[16] H. K. Boparai, M. Joseph, and D. M. O'Carroll, "Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles," *J. Hazard. Mater.*, vol. 186, pp. 458-465, 2011.

[17] W. J. Weber Jr. and J. C. Morris, "Kinetics of adsorption on carbon from solution," *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, vol. 89, pp. 31-60, 1963.



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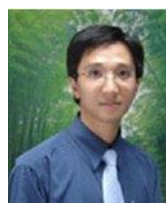
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