บทความวิจัย

Potential Adsorption of Leonardite for Heavy Metal Ions Removal from Aqueous Solution

Thinikan Thongkam[1], Khuanjit Hemavibool[1], Jintana Klamtet[1]
and Sairoong Ouypornkochagorn[1*]

Received: 7 July 2019
Revised: 20 July 2019
Accepted: 24 July 2019

ABSTRACT

The potential of leonardite as an adsorbent for the removal of heavy metal ions, Cu(II) and Mn(II), from aqueous solutions was investigated. The adsorption parameters, including pH and contact time, were optimized in the batch treatment process. The adsorption kinetics of leonardite for heavy metal ions were fitted to the pseudo-second-order model. Adsorption process for removal of Cu(II) was fitted to the pseudo-second-order kinetic model, while that of Mn(II) has followed the pseudo-first-order model. The adsorption of leonardite for both metals was fitted well with Langmuir and Freundlich isotherms. The maximum adsorption capacity was 41.67 and 11.57 mg g^{-1} for Cu(II) and Mn(II), respectively. The results indicated that leonardite waste materials could be employed as a promising adsorbent for removal of Cu(II) and Mn(II) ions from the industrial wastewater treatment process.

Keywords: Leonardite, Copper, Manganese, Heavy metals, Adsorption

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[1] Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, Thailand

[*] Corresponding Author: e-mail: sairoongo@nu.ac.th

Introduction

Leonardite is a low rank coal that cannot be used as fuel due to its low heating content. It is an oxidized form of lignite obtained from coal mines. Leonardite is medium brown, coal-like substance and often found at shallow depths [1-2]. However, its high content of humic acid is attributed to a general improvement of soil fertility [3-4]. Since humic acid contains several functional groups such as carboxyl, hydroxyl and carbonyl, it can act as carriers of polycyclic aromatic hydrocarbon (PAH) compounds [5-6]. These functional groups enable leonardite to have high cation exchange capacity for the removal of heavy metals [7-8]. The compositions of leonardite from various places were different. For leonardite from Mae Moh lignite mine, most works studied the applications of leonardite as fertilizer or studied the adsorption of cationic or anion dyes. There are only few works studied on the adsorption of heavy metals, e.g. arsenic, lead and zinc from this coal-mine [8-10].

In recent years, heavy metals such as arsenic, cadmium, lead, copper, manganese and chromium have become one of the most serious environmental problems. Heavy metals are found in the wastewaters from various industries such as battery manufacturing, metal plating facilities, pesticides and mining. Because of their high solubility in the aquatic environments, heavy metals tend to accumulate in living organisms. If the metals are ingested beyond the permitted concentration, they can cause various diseases and serious health disorders [11]. The excessive accumulation of copper in human body can cause vomiting, cramps, convulsions or even death [12]. Exposure to high levels of manganese has been associated with neuronal disorders, including Alzheimer's disease, Parkinson's disease, and amyotrophic lateral sclerosis [13]. Therefore, the removal of heavy metals like copper and manganese from contaminated wastewater before its discharge to the environment is necessary.

In this study, the removal of heavy metal ions from aqueous solution onto leonardite waste materials was investigated. The physical properties of leonardite were characterized by X-ray Diffractometer (XRD), X-ray Fluorescence spectrometer (XRF) and Scanning Electron Microscope (SEM). The adsorption parameters such as pH, contact time and adsorption isotherms were investigated. Moreover, the adsorption kinetics were also studied.

Materials and Methods

The adsorption solutions of copper and manganese were prepared from copper(II)nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (Carlo Erba) and manganese(II)nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) (AppliChem Co.). Nitric acid (HNO_3) was purchased from Merck and sodium hydroxide (NaOH) was obtained from RCI Labscan. 1000 mg L^{-1} Copper and manganese standard solutions were obtained from Loba chemie. All solutions were prepared with deionized water.

Leonardite (obtained from Mae Moh lignite mine, Lampang province, Thailand) was washed with deionized water, then dried at 110°C for 12 h, and then ground and the particles were passed through sieve between 200 and 325 mesh (45-75 μm). All cleaned leonardite were stored in desiccator for characterization and adsorption studies.

Leonardite characterization

The physical and chemical properties of leonardite were characterized by a powder XRD (PW 3040/60, X'Pert Pro MPD, PANalytical, The Netherlands) coupled with CuK_{α} radiation, dispersive X-ray fluorescence (WDXRF, Bruker S8 Tiger, Rigaku, Germany), Brunauer-Emmett-Teller (BET, Micromeritics TriStar ll 3020 surface area analyzer, Germany), Fourier transform infrared spectrophotometer (FTIR, Spectrum GX, Perkin Elmer, United States) in the range of 400-4000 cm^{-1} and a scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS, LEO 1455 VP, United Kingdom)

Batch adsorption experiments

The leaching of Cu and Mn and batch adsorption from leonardite were investigated. A 0.50 g of adsorbent was suspended into 50 mL of 15 mg L^{-1} Cu(II) and Mn(II) solutions and deionized water in 100 mL beaker. Then, pH of the solution was adjusted by 0.5 M HNO_3 or NaOH and stirred at 450 rpm for 30 minutes. Then the supernatants were filtered to remove the solid adsorbent and then analyzed the remaining metal ions by flame atomic absorption spectrometer (FAAS, Varian SpectrAA-220, United State).

The effect of pH was studied in a range of 2 to 6, while the effects of contact time and adsorption kinetics were studied in a range of 5 to 240 minutes [10].

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_e and q_e are the concentration (mg L^{-1}) of the metal and the amount of adsorbed metal on the surface of the adsorbent at equilibrium, respectively. C_0 (mg L^{-1}) is the initial concentration of the metal ion, V (mL) is the volume of solution and m (g) is the mass of the dry sorbent.

Two types of absorption kinetics are generally used and compared, namely the pseudo-first order and pseudo-second order rate laws. The pseudo-first-order kinetic model [10] was given by equations:

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

where q_t is the amount of solute adsorbed per mass of sorbent (mg g^{-1}) at any time (t) and k_1 is the rate constant of first-order adsorption (min^{-1}).

The pseudo-second order kinetic model was expressed by equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is second-order adsorption constant.

The adsorption isotherms of Cu(II) and Mn(II) were monitored in the range of 5 to 100 mg L^{-1} and calculated by the following equations [14-16]:

The Langmuir isotherm was calculated by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where q_m is the maximum adsorption capacity (mg g^{-1}) and K_L represents the Langmuir constant (L mg^{-1}).

The Freundlich isotherm was calculated by the following equation:

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

where K_f represents Freundlich isotherm constant (mg g^{-1}) and n is a Freundlich constant related to adsorption intensity.

Results and discussions

Physicochemical Characterization of adsorbent

The chemical composition, loss on ignition, surface area, pore volume and average pore size of leonardite were analyzed by XRF and BET. Leonardite from Mae Moh lignite mine consisted of SiO_2 (22.60%), Al_2O_3 (12.90%), SO_3 (8.72%), Fe_2O_3 (5.21%), CaO (2.02%), K_2O (1.36%), MgO (0.50%), Na_2O (0.34%) and TiO_2 (0.31%). The aluminosilicate (SiO_2 and Al_2O_3) is the major of composition of leonardite, along with traces of Fe, Ca, K, Mg, Na, Ti and S in the form of impurities. The results from BET showed surface area of 19.31 m^{-2} g^{-1}, pore volume of 6.50×10^{-2} cm^3 g^{-1} and the average pore size 13.47 nm. The XRD patterns (Figure 1) confirmed that leonardite mainly consisted of quartz, gypsum, montmorillonite, kaolinite and pyrite.

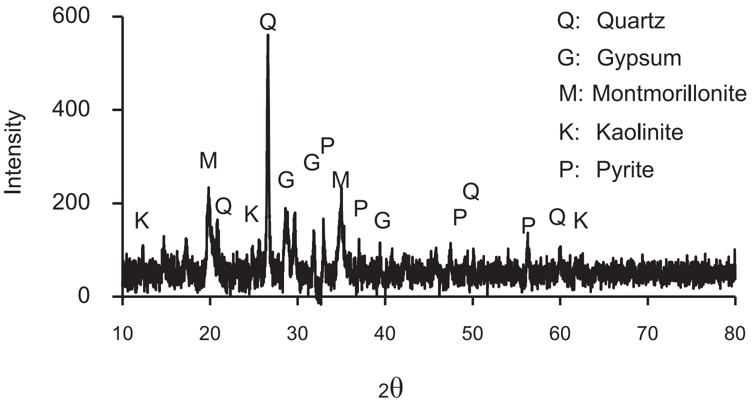

Figure 1 X-ray diffraction patterns of leonardite.

The FTIR spectra of leonardite (Figure 2) showed the signal of hydroxyl group (Si-OH, Al-OH) around 3697 and 3621 cm^{-1} and the appearance of O-H stretching and water deformation of -COOH at 3402 and 1680 cm^{-1}. The absorption bands at 2923 and 2852 cm^{-1} were ascribed to asymmetric and symmetric C-H bonding. The bands at 1619 and 1428 cm^{-1} were assigned to C=C aromatic ring from polyaromatics. The band at 1100-900 cm^{-1} of the Si-OH stretching vibration indicated the presence of inorganic silicate minerals, while the surface of leonardite from SEM micrographs in Figure 3 was a sheet-like morphology with multilayers coarse particle. It aggregated to form different size of particles in irregular shape.

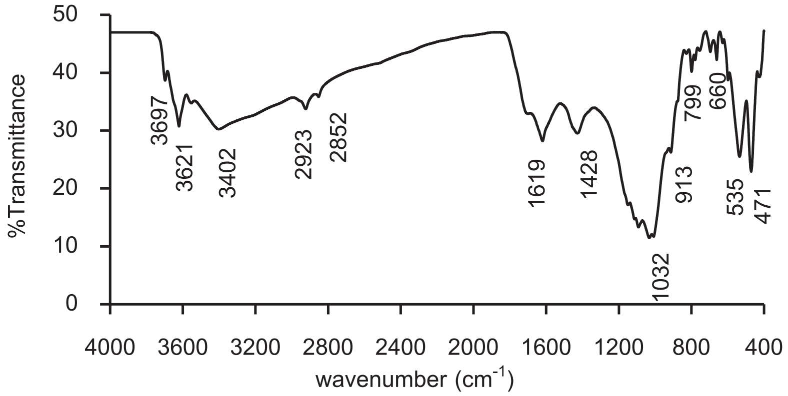

Figure 2 FTIR spectra of leonardite.

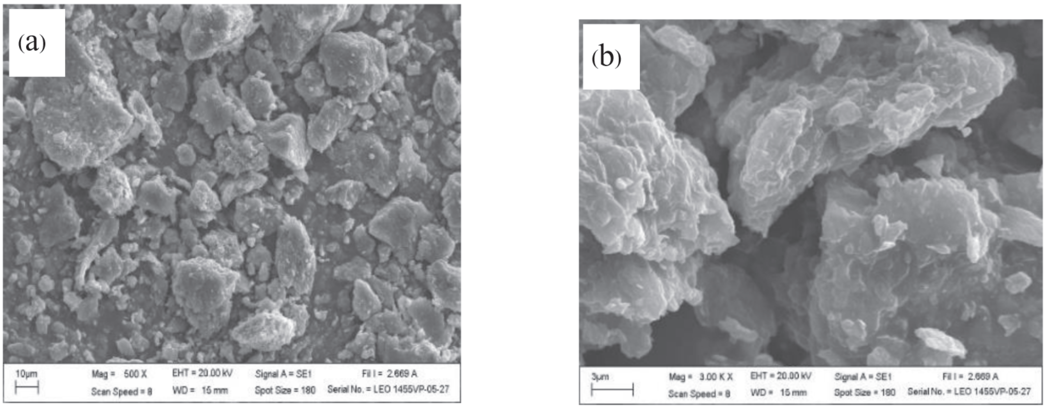

Figure 3 SEM morphology of leonardite (a) 500× and (b) 3000× magnifications.

The effect of pH and contact time to the metal adsorptions

The pH of the aqueous solution and contact time were important factors on heavy metal ions removal [17-18]. The effect of pH on the adsorption of Cu(II) and Mn(II) was shown in Figure 4. Both metals were the same adsorption efficiencies. They were increased and reached maximum removal at pH 6 as same as other adsorbents [19-20], It is due to the high H^+ concentration present at lower pH. Hydronium ions have competed with metal ions during removal process while Cu(II) and Mn(II) were precipitated at pH > 6. The leaching of Cu(II) and Mn(II) was not found from leonardite from any condition.

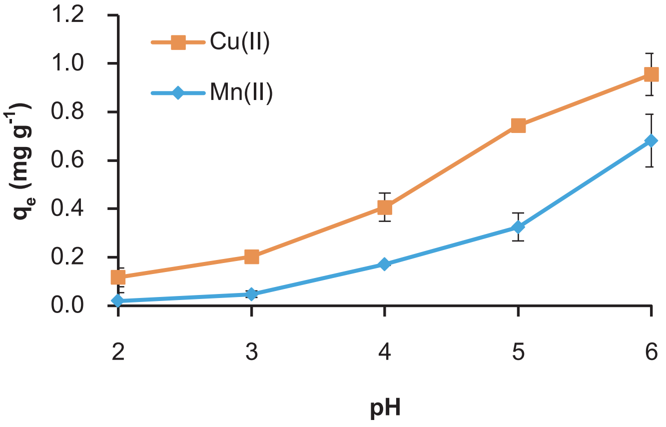

Figure 4 Effect of pH on 15 mg L^{-1} of Cu(II) and Mn(II) adsorption for 30 minutes.

The effect of contact time and kinetics

The effect of contact time was indicated in Figure 5. The results showed that during 30 minutes, percentage removal of Cu(II) and Mn(II) was increased significantly with increasing time due to the large available surface area of adsorbent and rapid surface adsorption. After this period, the adsorption rates were slightly increased until an equilibrium point after 120 minutes. Therefore, the optimized conditions of Cu(II) and Mn(II) adsorption by 0.5 g of leonardite were operated under pH 6 for 30 minutes.

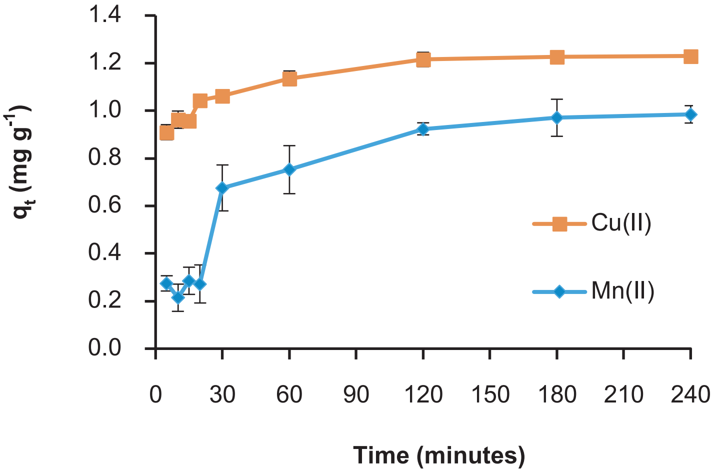

Figure 5 Effect of contact time on 15 mg L^{-1} of Cu(II) and Mn(II) adsorption under pH 6.

In addition, the pseudo-first-order and pseudo-second-order kinetic models of both metals onto leonardite were described in Figure 6 and Table 1. Cu(II) and Mn(II) were fitted to both pseudo-first-order and pseudo-second-order models. However, the correlation coefficient (R^2) and $q_{e, exp}$ showed that the adsorption of Cu(II) by leonardite followed the pseudo-second-order model better than pseudo-first-order model. Thus, the pseudo-second-order model was more appropriate to describe the adsorption kinetic behaviors for Cu(II) and Mn(II) onto the amount of leonardite and the chemisorption was the rate controlling step [21].

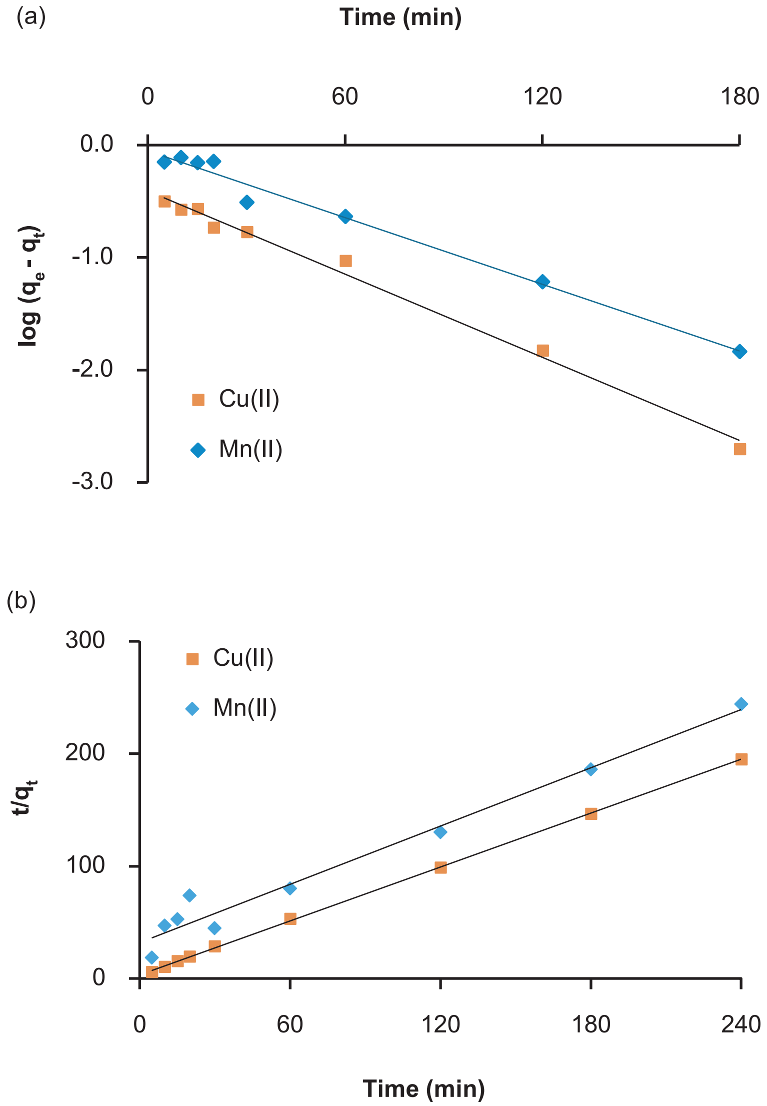

Figure 6 The (a) pseudo-first order and (b) pseudo-second order models for adsorption of 15 mg L^{-1} of Cu(II) and Mn(II) under pH 6.

Table 1 Kinetic parameters of pseudo-first order and pseudo-second order models for adsorption of Cu(II) and Mn(II).

Kinetic models	Parameter	Heavy metal ions	
		Cu(II)	Mn(II)
Pseudo-first-order	$q_{e,exp}$ (mg g^{-1})	1.23	0.98
	$q_{e,cal}$ (mg g^{-1})	0.33	0.02
	k_1 (min^{-1})	2.28×10^{-2}	2.28×10^{-3}
	R^2	0.9923	0.9846
Pseudo-second-order	$q_{e,cal}$ (mg g^{-1})	1.25	1.16
	k_2 (g mg^{-1} min^{-1})	0.99	2.48×10^{-2}
	R_2	0.9998	0.9717

The adsorption isotherm of heavy metals

The adsorption isotherms were obtained using 5-100 mg L^{-1} Cu(II) and Mn(II) solutions at pH 6 with stirring rate of 450 rpm for 120 minutes. The Langmuir and Freundlich parameters were presented in Table 2. Comparing the correlation coefficient (R^2) for the Langmuir and Freundlich models, it is verified that the adsorption data of Cu(II) on the leonardite was fitted well to Freundlich models while Mn(II) was fitted to Langmuir model. According to Langmuir equation, the maximum adsorption capacity for the metals were found to be 41.67 and 11.57 mg g^{-1} of Cu(II) and Mn(II), respectively. However, the correlation coefficient of Cu(II) was more fitted to Freudlich than Langmuir model while the correlation coefficient of Mn(II) was not significantly different. The sum of square error (SSE) of Langmuir isotherm and Freundlich isotherm of Cu(II) by ANOVA ($p = 0.05$) were 0.65 and 0.34, respectively and the SSE of the Langmuir and Freundlich models of Mn(II) were 1.84 and 0.20, respectively. It confirmed that the adsorption of Cu(II) and Mn(II) were fitted to Freundlich model. These results confirmed the adsorption of both metals on heterogeneous surfaces. Compared to the adsorption of Cu(II) by leonardite from Spain, the maximum adsorption capacity of Cu(II) by leonardite from Thailand was higher than that from Spain (20.97 mg g^{-1}) [22]. It showed that leonardite from Thailand was more effective than leonardite from Spain.

Table 2 Parameters of Langmuir and Freundlich models for the Cu(II) and Mn(II).

Heavy metal ions	Langmuir isotherm			Freundlich isotherm		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f (L mg^{-1})	n	R^2
Cu(II)	41.67	0.02	0.96	1.03	1.31	1.00
Mn(II)	11.57	0.05	0.97	0.08	1.45	0.96

Conclusions

Leonardite can be used for adsorption of Cu(II) and Mn(II) ions from aqueous solutions. The adsorption of heavy metal ions was pH and contact time dependent. Adsorption of Cu(II) onto leonardite fitted to pseudo-second-order kinetic model, while pseudo-first-order fitted better for Mn(II) adsorption. In addition, adsorption isotherm of leonardite can be modeled by both Langmuir and Freundlich isotherms. The capacity of leonardite for adsorption of heavy metal ions can be calculated by using these models. The order of the removal of heavy metal ions was Cu(II) > Mn(II).

Acknowledgements

This work was financially supported by the National Research Council of Thailand. The author would like to thank Department of Chemistry and Science Laboratory Center, Faculty of Science, Naresuan University for instrument support along this study.

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