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Removable Pb (II) from aqueous solutions by adsorption onto natural and modified leonardite

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Abstract

Natural leonardite was modified with manganese nitrate. The chemical composition, physical properties and adsorption efficient of natural and modified leonardite were investigated. The chemical composition was characterized by X–ray fluorescence spectroscopy (XRF) and energy dispersive X–ray spectrometry (EDXS). Physical properties, morphology and surface area were investigated by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller analyzer (BET). The adsorptions of Pb(II) onto natural and modified leonardite was determined by atomic absorption spectroscopy (AAS). The results of XRF and EDXS were showed that silicon was major element. The surface area of natural leonardite was 22.90 $m^2 \cdot g^{-1}$ which less that the surface area of modified leonardite, 31.02 $m^2 \cdot g^{-1}$. The Pb(II) adsorption data of natural and modified leonardite was fit well with the Langmuir isotherm equation. The maximum monolayer adsorption capacity of Pb(II) onto natural and modified leonardite was found to be 3.098 $mg \cdot g^{-1}$ and 7.062 $mg \cdot g^{-1}$ respectively. It was presented that the percentage of maximum adsorption capacity increase to 127.95.

Keywords: Adsorption, Natural leonardite, Modified leonardite, Lead, Manganese

1. Introduction

At present, increased usability of heavy metals in manifold industrial processes is causing an increased wastewaters contaminated with these non–degradable toxic ions, which reach to environment [1]. The existence of non–degradable toxic ions in the biological systems and cumulate within the bio–system as these toxic ions move to the food chain [2]. Specific symptomatology diverge according to the quantity of metal, the total dose absorbed and the exposure was acute or chronic, if lead was ingested several times, may influence developmental processes, brain damage and behavioral disorders [3]. The technology of adsorption is widely used for the heavy metals removal from aqueous solutions. Leonardite is low cost material and can adsorb heavy metal ion [4]. There are silicon dioxide and humic acid which consist of organic compounds [5]. Recently, humic acid was used enhance efficiency for removal Cu (II) from aqueous solution [6]. However, manganese is one of enhancement material, it has been showed excellent adsorption properties for the removal of heavy metal ions from aqueous solution [7], abundance of single bond OH functional groups capable of reacting with adsorbed metal ions [8]. So, the study of enhance efficiency of leonardite adsorbent by manganese and Pb (II) adsorption is one alternate to remove heavy metals from environment. Low temperature process was used for preparation of manganese modified leonardite. The properties of natural and modified leonardite are characterized by XRF, EDXS, SEM and BET. The concentration of Pb (II) from aqueous solution by adsorption onto natural and modified leonardite was determined by AAS.

2. Materials and methods

Natural leonardite was obtained from Mae Mao mine coal, Lampang, Thailand. It was sieved to 200 mesh, dry at 90 ºC with hot air oven (Honeywell–DC1040, Thailand) 12h and stocked in desiccator. Manganese modified process was applied by using low temperature and slow removing water [1]. Leonardite 10 g was added with 0.1 M HNO_3 in flask, shaked 12h at room temperature and dried at 90 ºC. $Mn(NO_3)_2 \cdot 4H_2O$ was diluted to 100 ml, pH 9 in the flask. After that, a both flasks were mixed. This mixture was shaken in the water bath with the slow speed at 70 ºC and was taken into beaker and immediately dried at 90 ºC in the

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drying oven when the mixture had remained 10%. The modified leonardite sample was cooled, washed several times, dried at 90 ºC and was stored in desiccator. The chemical compositions of natural and modified leonardite were characterized by XRF (Horiba–MESA 500W) and EDXS (ISIS300, Oxford, UK). The morphology was investigated by SEM (Jeol–JSM5910LV, Japan). The surface area of these adsorbents were measured by BET (Quantachrome–Autosorp 1MP, England). Batch adsorption studies were implemented by shaking 0.1 g of sample with 50 mL of the aqueous solution of Pb(II) at pH 5 for 1h at room temperature. The concentration of Pb(II) after adsorption was determined using flame atomic absorption spectrometer (PerkinElmer–AAnalyst100, U.S.A.).

3. Results

The result of XRF showed that silicon dioxide (SiO_2) was major component of natural (46.32 %) and modified leonardite (47.47 %). Other metal oxides (Al_2O_3 and Fe_2O_3) are the minor constituents and corresponded with the previously report [9]. However, manganese dioxide (MnO_2) was found in modified leonardite (11.51 %).

The result of EDXS showed the value for silicon of K_α = 1.80 keV of natural and modified leonardite (Figure 2 (a) and (b)). However, the energy value for manganese of K_α = 5.90 keV (Figure 2 (b)) was showed in modified leonardite. After adsorption, result of EDXS showed that Pb(II) was found in natural and modified leonardite at M_α = 2.34 keV (Figure 2 (c) and (d)).

SEM micrographs of natural and modified leonardite were showed in Figure 1. The morphology of both leonardite was sheet in shape with the range of particle size of 1–5 μm in width and length. The surface area of modified leonardite was 31.02 $m^2 \cdot g^{-1}$ which higher than natural leonardite, 22.90 $m^2 \cdot g^{-1}$ and leonardite of 19.9 $m^2 \cdot g^{-1}$ from the previously reported [10]. It is found that the surface of Mn on modified leonardite has more surface area than hydroxyl groups from natural leonardite [11].

(a)
(b)

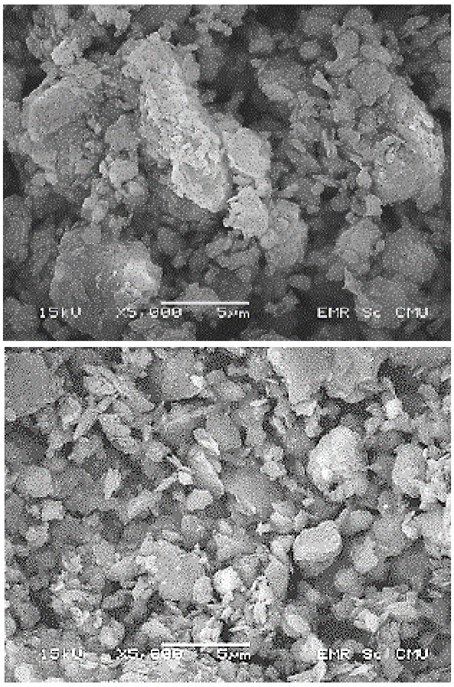


Figure 1 SEM micrographs of (a) natural leonardite and (b) modified leonardite

Adsorption isotherms of Pb (II) onto natural and modified leonardite are showed in Figure 3 (a). This adsorption isotherms resemble monolayer adsorption form, accordance with the classification of adsorption isotherms. As showed, The amount of Pb(II) adsorbed increases with raising of Pb(II) concentration until a maximum adsorption is limited. Moreover, this isotherm shows that adsorption capacity of leonardite is greatly improved by modification with manganese. The model which monomolecular layer of adsorbate is attracted with the adsorbent surface. The adsorption of monolayer is distinguished by the matters of fact that the maximum adsorption value at moderate concentration. The famous equation is the Langmuir equation [12].

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

where q_e is the surface concentration or amount adsorbed per unit mass of adsorbent ($mg \cdot g^{-1}$), q_m is the maximum adsorption capacity ($mg \cdot g^{-1}$), C_e is the equilibrium concentration of Pb (II) ($mg \cdot L^{-1}$), and K_L is the Langmuir constant or equilibrium constant ($L \cdot mg^{-1}$).

(a)
(b)
(c)
(d)

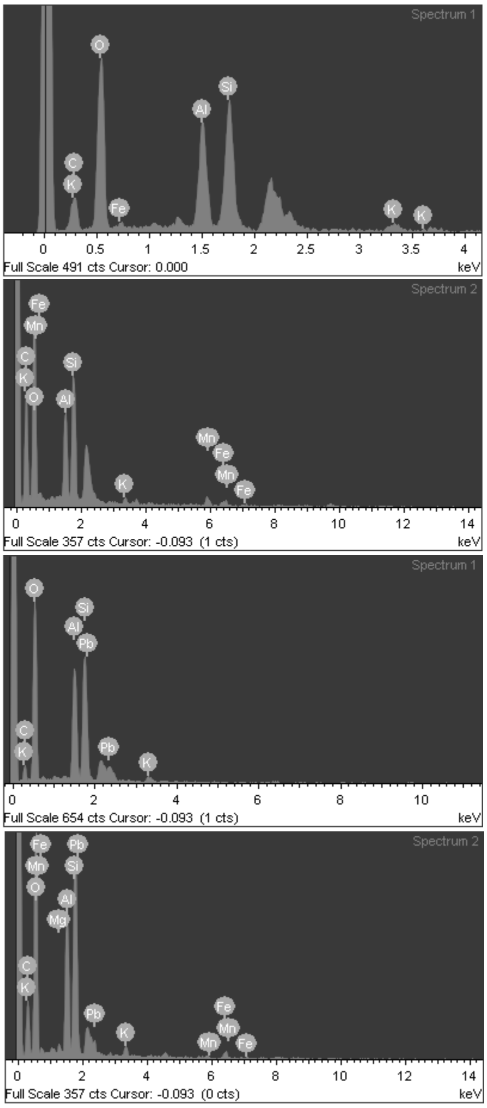
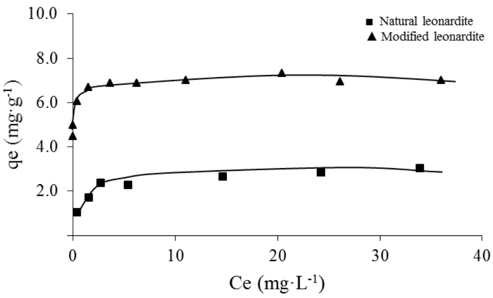
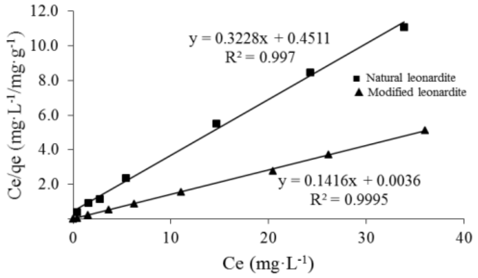


Figure 2 EDXS of natural and modified leonardite before (a), (b) and after (c), (d) adsorption Pb (II) 50 ppm, pH 5, at room temperature



(a)



(b)

Figure 3 Adsorption isotherm (a) and Langmuir isotherm (b) for the adsorption of Pb(II) onto natural leonardite and modified leonardite

Langmuir isotherms of Pb (II) onto natural and modified leonardite are showed in Figures 3 (b). The maximum adsorption capacity of natural and modified leonardite are 3.098 and 7.062 mg·g^{-1}. This result demonstrates the higher capacity of modified leonardite for Pb(II) removal as compared to natural leonardite.

4. Discussion

At the surface of leonardite, the structure terminates consist of either siloxane group (Si–O–Si) or silanol groups (Si–OH) are importance in adsorption applications [13]. However leonardite abundance of humic acid which consist of carboxylic acid, phenolic hydroxy, enolic and alcoholic group [14]. These groups can adsorb and coordinate the heavy metal ions forming chelate, internal ring structure, which is forming complexation [15]. Furthermore, manganese encourage improving adsorption efficiency of adsorbent. For modified leonardite, the result of surface charge presented by formation of manganese oxides of Mn on leonardite surface which surface charge of manganese oxides is higher than SiO_2 and Al_2O_3, because of the large acidity constant of manganese oxide surface [16].

5. Conclusions

Natural leonardite was modified by manganese nitrate tetrahydrate via the low temperature. The chemical composition of modified leonardite was showed manganese dioxide which correspond with the result of EDXS. The BET results were suggested that higher the specific surface area, possessed by the manganese modified natural leonardite. The percentage of maximum adsorption capacities of modified leonardite higher than natural leonardite.

6. Acknowledgements

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