Adsorption of Zinc Ion on Leonardite Prepared from Coal Waste

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ABSTRACT

Naturally occurring leonardite, obtained from Mae Moh mine lignite, has been tested as a potential sorbent for Zn^{2+}. The factors that affect to the sorption, such as pH, contact time and the adsorption isotherm were also investigated. The high performance of Zn^{2+} removal was demonstrated at pH values of 5-6. Batch experiment showed that the equilibrium was reached after 180 min. The sorption data were correlated with the Langmuir and Freundlich adsorption models. The average maximum adsorption capacity was found to be 0.141 mmol g^{-1}. Moreover, the equilibrium parameter, K_R indicated the favor ability of leonardite for adsorbed Zn^{2+}.

Key words: wastewater; adsorption; zinc; leonardite; coal waste

INTRODUCTION

Heavy metal like zinc (Zn) is often found in plating, galvanizing and roller coating operations [1]. Althoughzinc is essential minerals but too much is not beneficial. The increase of zinc concentrations above the consent limits is becoming an important subject to public health [2]. Adsorption techniques employing solid sorbents provide an attractive alternative for the treatment of wastewater, especially if the sorbent is inexpensive and does not require an additional pre-treatment step (such as activation) before its application.

Leonardite or oxihumolite originated on the surface of lignite deposits by post-sedimentary oxidation. The oxihumolites, similarly to the related organic deposits such as humalites, are exploited for an industrial preparation of humic acids as well as additives to agricultural fertilizers [3-5]. Humic materials are complex organic molecules that contain a wide variety of functional groups: carboxyl (COOH), hydroxyl (OH) and carbonyl (C=O) that can be involved in chemical binding. Because of these properties, leonardite tends to have a high cation exchange capacity [6, 7]. The low-cost and the availability of this material make it a promising

candidate for pollution remediation in both soils and groundwater. Therefore, the adsorption of zinc on untreated leonardite from the Mae Moh lignite mine in Lampang province was studied. The adsorption capacities can be estimated from the parameters of the adsorption isotherms, and factors influencing the adsorption are investigated.

MATERIALS AND METHODS

The sorbent ¾leonardite¾obtained from the Mae Moh lignite mine in Lampang province, Thailand, was used without any additional pre-treatment except of grinding and size classification by sieving (80 mesh). The surface area determined by the Brunauer-Emmett-Teller (BET) method using a Quantachrome Autosorb automate with nitrogen gas (version 2.46), after drying at 110C for 12 hours was in the range 18.94-26.29 m^2 g^{-1}, and the average cation exchange capacity (CEC) measured to evaluate the adsorption capacity by the ammonium acetate method was found to be 61.95 cmol kg^{-1}.

All reagents used are AR grade and heavy metal stock solutions were prepared with concentrations of up to 1000 mg/L of zinc nitrate salt in deionized water. The stock standard solution of zinc ion at concentration of 1000 mg/L was obtained from Fluka, Buches, Switzerland. Working standard solutions were obtained by appropriate dilution of the stock standard solution. Solutions of nitric acid (0.5 M) and sodium hydroxide (0.5 M) were used for pH adjustment.

Determination of zinc ion in the initial and remaining solutions was carried out by atomic absorption spectrophotometer, series AA-275, Varian Company, Australia.

Influence of pH on Zn^{2+} adsorption

The effect of pH on the adsorption of Zn^{2+} by leonardite was studied with aqueous solutions of zinc ion at 5 and 20 mg/L concentrations. The initial pH was adjusted to pH 2, 3, 4, 5 and 6 with nitric acid (0.5 M) or sodium hydroxide (0.5 M) solutions. Then, 0.4 g of the leonardite was added to flasks containing 50 mL of the zinc solutions. The flasks were maintained under continuous agitation for 24 h, at room temperature and 130 rpm. Then,

the mixture was centrifuged and filtered, and the remaining zinc ion concentrations were determined.

A blank was prepared by adding 0.4 g of leonardite to 50 mL of DI water to verify whether the leonardite transferred zinc ion to water. Control test solutions (10 mL) were filtered and analyzed after pH adjustment to ensure that no precipitates formed prior to contact with the sorbent.

Effect of contact time

Batch experiments were conducted to determine the time needed to reach equilibrium at the optimum pH. 0.4 g leonardite was added to flasks containing 50 mL of 5 and 20 mg/L of Zn^{2+} aqueous solutions. The experimental conditions used were the same as those mentioned above. Samples were collected at various periods of time (10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360 min), each mixture was centrifuged and filtered, and the remaining metal ion concentrations were determined.

Adsorption Isotherm

To test the adsorption capacity of leonardite, the experiments were carried out with aqueous solutions of Zn^{2+} at initial concentrations from 5 to 100 mg/L, with 0.4 g leonardite dose. The flasks were kept in the same conditions as described above until equilibrium time, and the Zn^{2+} concentrations were determined in the remaining solutions.

RESULTS AND DISCUSSION

Effect of pH

The adsorption of Zn^{2+} by leonardite was studied at a pH range of 2-6 for a fixed 0.4 g of leonardite, in order to investigate the optimum pH for the removal of Zn^{2+}. The amount of Zn^{2+} removed for each pH was calculated by comparing the initial concentrations of Zn^{2+} with that remaining in the solution after 24 h. For the analysis of Zn^{2+} in blank solutions showed that there was no leaching of them from the adsorbent. Fig. 1 shows the removal of Zn^{2+} versus initial pH for a fixed adsorbent dose and initial concentrations of 5 mg/L and 20 mg/L. As can be seen, the removal of Zn^{2+} from aqueous solutions by sorption on leonardite was pH dependent. By increasing the pH from 2 to 6 the

adsorption increased 43% (for 5 mg/L), and to 40% (for 20 mg/L). It has been reported that at pH 2, the adsorption of Zn^{2+} on leonardite was practically negligible [8, 9]. The pH effect of adsorption on leonardite can be explained by the surface characteristics of the adsorbent. H^+ ions affect metal complexation because they have a great affinity for

many complexing and ion-exchange sites. At low pH functional oxidized groups (hydroxyl, carboxyl, phenol, methoxy, etc.) of humic acids are protonated. This phenomenon would be the competition between H^+ and zinc ions for sorption on the leonardite surface sites, leading to poor removal of Zn^{2+}. As the pH increases Zn^{2+} will replace

Table 1: Langmuir constants for Zn²⁺ isotherm

	C_e(mg L⁻¹)	q_e(mg g⁻¹)	C_e/q_e(g L⁻¹)	q_{max}(mg g⁻¹)	K_L(g⁻¹mg)	R^2
			Langmuir Isotherm			
Zn²⁺	2.08	0.348	5.97			
	4.54	0.680	6.67	9.19	0.018	0.9483
	9.23	1.29	7.16			
	14.09	1.90	7.43			
	19.51	2.42	8.07			

Table 2: Freundlich constants for Zn²⁺ isotherm

	$log\ C_e$	$log\ q_e$	K_F(mg L⁻¹)	n	R^2
			Freundlich Isotherm		
Zn²⁺	1.15	0.278			
	1.29	0.383	0.301	1.4	0.9892
	1.51	0.532			
	1.63	0.653			
	1.77	0.695			

hydrogen ions from the surface of the leonardite and therefore the extent of the adsorption increases [9-11].

Contact time

The percentages of Zn^{2+} removal against contact time at the optimum pH value 6and with initial concentrations of 5 and 20 mg/L are shown in Fig. 2. Adsorption first follows, an initial rapid process, and the stationary state was observed from 120 min of contact with Zn^{2+} concentration of 5 mg/L, while at higher initial Zn^{2+} concentration of 20.00 mg/L, the time necessary to reach equilibrium was after 120 min. For the initial faster rate of metal transition may be explained by the large, uncovered available surface area of the leonardite. The slower adsorption rate in the second phase is probably due to the diffusion of metal ions into the porous

structure of the leonardite [1]. If the adsorption materials contain large numbers of oxygen functional groups means that the functional groups act initially as metal coordination sites. However, the experimental data were measured at 180 min to be sure that full equilibrium was achieved.

Sorption equilibrium: adsorption isotherms

The adsorption isotherm was measured for the initial Zn^{2+} concentrations ranging from 5.00 to 100.0 mg/L. The tests were carried out for a contact time of zinc ion and 0.4 g L⁻¹ of leonardite dose. The amount of metal ion adsorbed at equilibrium per unit mass of leonardite (q_e, mg g⁻¹) was calculated using the following equation:
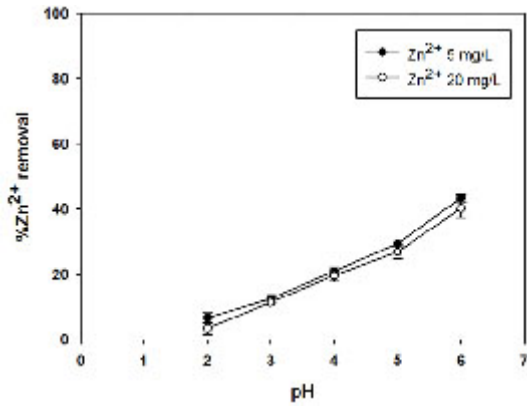
$$q_e = (c_i - c_e)\frac{V}{m} \qquad (1)$$

Fig.1 : Effect of pH on Zn^{2+} onto leonardite at concentrations of 5 mg/L and 20 mg/L
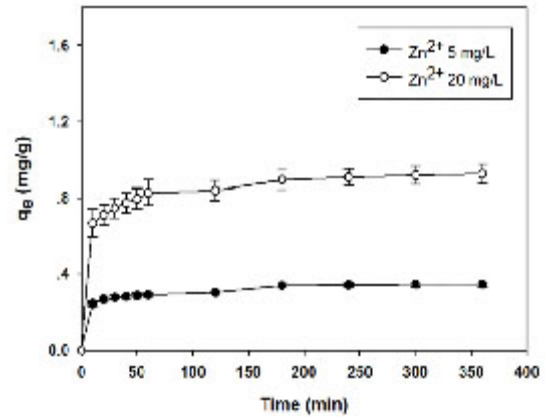

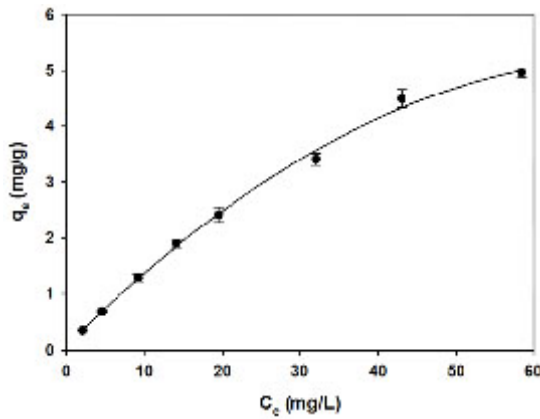**Fig. 2: Adsorbed amount vs. time for Zn^{2+}atconcentrations of 5 mg/L and 20 mg/L**
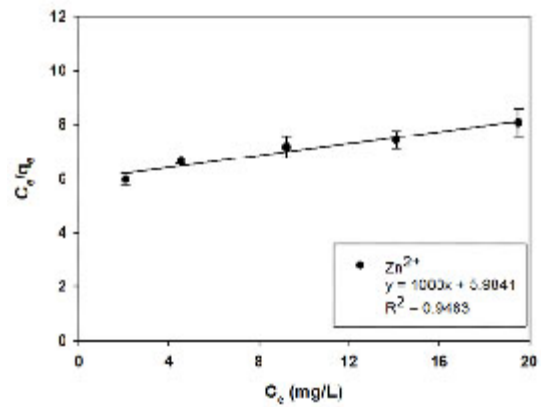

Fig.3 : Adsorption isotherm for Zn^{2+}on leonardite
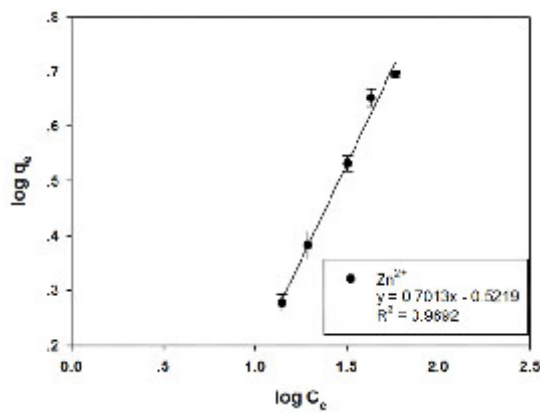

Fig. 4 :Langmuir isotherm of Zn^{2+}
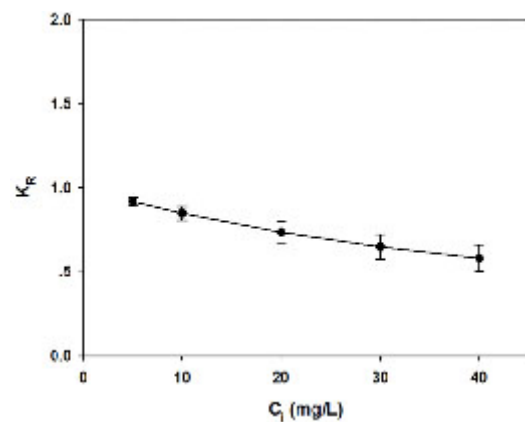

Fig. 5: Freundlich isotherm of Zn^{2+}

Fig.6 : Plots of K_R versus the initial concentration, C_i, of Zn^{2+}

where C_i (mg L^{-1}) is the initial metal concentration, C_e (mg L^{-1}) is the final (equilibrium) metal concentration, V (L) is the solution volume and m (g) is the mass of adsorbent. Fig. 3 shows the adsorption isotherm of Zn^{2+}.

The Langmuir and Freundlich isotherms, which have been extensively used to describe of the adsorption process in different metal-sorbent systems, were used to analyzed the relationship between the adsorption capacity of leonardite and Zn^{2+} concentrations at equilibriumin the present study. The equations of the Langmuir(Eq. (2)) and Freundlich (Eq. (3)) isotherms are represented as:

$$q_e = \qquad \qquad (2)$$

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \qquad (3)$$

where q_{max} and K_F indicate the adsorption capacity of leonardite, n and K_L are related to adsorption intensity. The constant values of the both isotherms can be calculated from the linearized forms of Eqs. (4) and (5) represented by:

$$\qquad \qquad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

Table 1 and 2 show the calculated Langmuir and Freundlich constants and the corresponding coefficients of correlation values of Zn^{2+}. The experimental data were fitted to the Langmuir isotherm from an equilibrium concentration of 2.08 mg/L (Fig. 4) and the Freundlich isotherm up to an equilibrium concentration 60 mg/L (Fig. 5). According to the Langmuir equation, the maximum adsorption capacities for Zn^{2+} was 9.19 mg g^{-1} (0.141 mmol g^{-1}). From Table 2, the Freundlich constant of Zn^{2+}, n, is greater than unity (n = 1.4) indicating favorably adsorption of Zn^{2+} on leonardite. Furthermore, the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R, define as:

$$K_R = \qquad \qquad (6)$$

where K_R is a dimensionless separation factor. The value of K_R indicates the shape of the isotherm to be unfavorable ($K_R > 1$), linear ($K_R = 1$), irreversible ($K_R = 0$) or favorable ($0 < K_R < 1$) [11-13]. The value of K_R for Zn^{2+} is given in Fig. 6. The K_R values of Zn^{2+} is less than 1 indicated that the sorption on leonardite is favorable.

Due to the heterogeneous nature of humic substances, the complexation of Zn^{2+} to humic material can be regarding as occurring at the reactive sites with binding affinities that range from weak forces (i.e. ionic) of attraction to formation of highly stable coordinate linkages. In Fig. 7 the structures of types III, IV represent the predominant forms of complexed Zn^{2+} when humic material are

Fig. 7 : Example of Zn^{2+} binding to humic material

present in abundance. Binding at the weaker sites (I and II) become increasingly important as the stronger sites become saturated. However, explanation of the sorption mechanism is unlikely to be so simple, because of the complex heterogeneous nature of leonardite, together with the abundance of functional groups present in leonardite.

CONCLUSION

In this study, leonardite from Mae Moh mine could be able to adsorbed Zn^{2+} aqueous solution. The adsorption in these systems is pH dependent, and the best results were obtained in the pH range 5-6. It would indicate that the ion exchange and metal complexation reaction took place in the metal removal with leonardite. The experimental data in the linear form of Langmuir and Freundlich equations gave satisfactory correlation coefficients and concentration ranges. The average maximum

adsorption capacity was 0.141 mmol g^{-1}. The advantage of leonardite sorbent in this study is that it can be used in crude form without pre-treatment step, low cost and is available in large quantities, which makes leonardite a promising candidate for wastewater treatment and further development improved.

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