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Removal of Pb(II) from Aqueous Solution Using Tremolite Amianthus

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Tremolite amianthus was characterized and studied for the removal of Pb^{2+} from aqueous solution through batch equilibrium experiments. Scanning electron microscope (SEM) was used to observe the surface properties of the tremolite amianthus. To highlight their application, selected information on time, pH, initial metal concentration and adsorption capacity of tremolite amianthus are investigated. Adsorption behavior of Pb^{2+} ions was described with the Langmuir and Freundlich equations. The adsorption capacity of tremolite amianthus for Pb^{2+} was determined from the isotherms equations at different temperature. The thermodynamic parameters (ΔGº, ΔHº and ΔSº) were also determined and the adsorption process is more favoured at lower temperatures.

Key Words: Tremolite amianthus, Pb^{2+}, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

The water polluted by heavy metals is currently a matter of great concern and various treatment technologies have been developed for the removal of heavy metals from wastewater. The technologies commonly used to remove metal ions from effluents include chemical precipitation, lime coagulation, ion exchange[1-3], electro dialysis, reverse osmosis membrane filtration[4-6], electro winning[7], solvent extraction and common adsorption[8-10]. Compared with other processes, the latter process is a more useful method for the metal removal[11,12].

Metal adsorption on substrate materials is considered to be the most suitable and economical method of removal[13]. Natural adsorbents such as zeolites, chitosan and clay has been most commonly employed for this goal, with great advantages. Tremolite amianthus belongs to the amphibole clay and has large surface, so it has a strong physical adsorption. To our best of knowledge, no other studies have been conducted for tremolite amianthus adsorption of heavy metal ions in aqueous solution.

EXPERIMENTAL

The natural tremolite amianthus sample was supported by Non-metallic Mining Co. Ltd. of Jiacheng, Zhejiang in China.

Procedure: Experiments were performed using a batch equilibrium technique by placing 0.1 g of adsorbent in flasks containing 100 mL of Pb^{2+} stock solution. All chemicals used in this study were analytical reagent grade. Different concentrations of Pb^{2+} stock solution were prepared by dissolving different qualities of $Pb(NO_3)_2$ in distilled water. Hydrochloric acid used for the pH adjustment were prepared by using concentrated HCl.

Photomicrography of the exterior surface of tremolite amianthus was obtained by SEM (JEOL6335F-SEM, Japan).

The adsorption of Pb^{2+} by tremolite amianthus was studied by a batch operation, including effect of contact time, the solution pH, temperature and initial metal ion concentration. Batch sorption experiments were carried out by shaking the flasks containing 100 mL of Pb^{2+} solutions and 0.1 g of the adsorbents at 220 rpm for a period of time using a water bath cum mechanical shaker. After that, the suspensions were centrifuged at 3000 rpm for 10 min. The supernatants were then collected and analyzed for Pb^{2+} concentration by a flame atomic adsorption spectrophotometer (Varian, Spectr AA 240 with air-acetylene oxidizing flame). Batch experiments were carried out by taking pH from 2-6 for Pb^{2+}, interaction time from 5-40 min, Pb^{2+} concentration from 30-500 mg/L and temperature of 20-55 ºC.

RESULTS AND DISCUSSION

Compared with different natural adsorbents: The adsorption capacities of different natural adsorbents (diatomite, natural zeolite, sepiolite amianthus, bentonite, kaolinite, tremolite amianthus and vermiculite) were shown in Fig. 1. (The sorption experiments were carried out at 20 ºC by shaking the flasks containing 100 mL of 50 mg/L Pb^{2+} solutions which pH is 6 for 0.5 h and 0.1 g of the adsorbents).

From the results shown in Fig. 1, it was obvious that tremolite amianthus is the appropriate sorbent fot lead ions. In the following, the adsorption properties of lead ions by tremolite amianthus will be investigated in details.

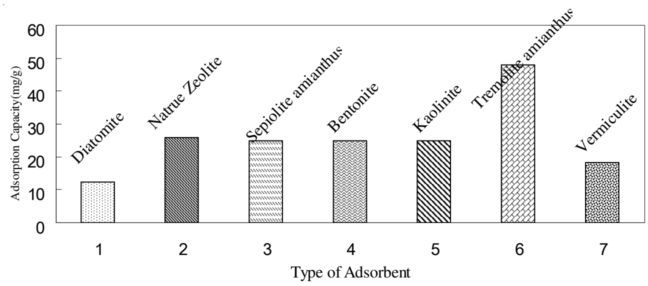
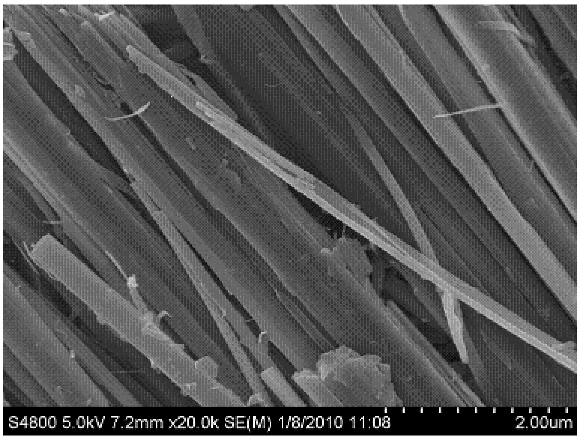
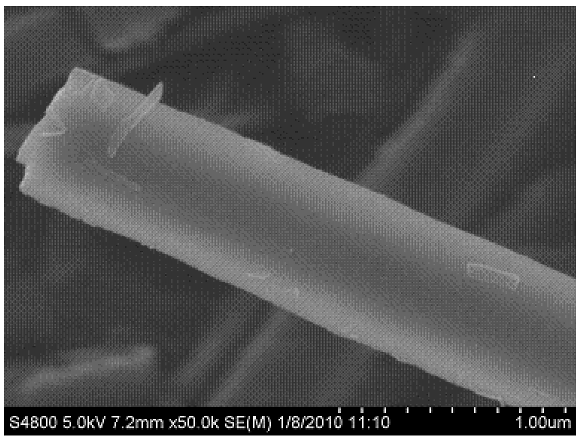


Fig. 1. Compared with different natural adsorbents

SEM analysis: The SEM micrographs of the tremolite amianthus were shown in Fig. 2. Fig. 2(a-b) were, respectively got in different magnification. It was observed that the shape of tremolite amianthus was mainly formed by dense sheets with a big surface, which were favourable for the adsorption of Pb^{2+}.



(a)



(b)

Fig. 2. SEM micrograph of Tremolite amianthus

Effects of time, temperature and adsorption kinetics: Stock solution of 500 mg/L of the standardized Pb^{2+} whose pH is 6 was prepared from $Pb(NO_3)_2$. The relationship between contact time and amount of Pb^{2+} adsorbed affected by temperature was shown in Fig. 3.

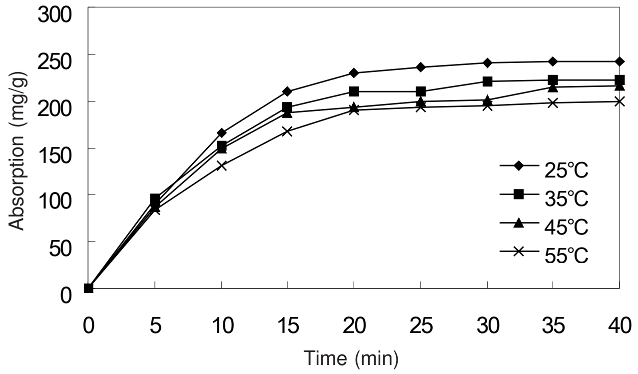


Fig. 3. Effect of contact time on the adsorption of Pb(II) on tremolite amianthus at various temperatures

It was observed that initial adsorption of Pb^{2+} was rapid on tremolite amianthus. The amount of Pb^{2+} uptake increased with contact time. At the beginning of the adsorption process, adsorption was fast because it was controlled by the exterior surface of the tremolite amianthus. The absorbed amount decreased with temperature from 25-55 ºC at the same time. According to the results of the experiments, the best temperature was 25 ºC.

The adsorption of Pb^{2+} onto tremolite amianthus may include a chemical sorption which implies the strong electrostatic interaction between the negatively charged surface and Pb^{2+}. Unuabonah *et al.*[14] developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat. The linear form of the diffusion equation is described in the following form:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \quad (1)$$

where Q_t is the amount (mg/g) of material adsorbed at time t, Q_e is the adsorption capacity (mg/g) at equilibrium and k is the rate constant (g/(mg min)) of pseudo-second-order model. The initial sorption rate h (mg/(g min)) was obtained according to eqn. 2, as t/Q_t approaches zero.

$$h = kQ_e^2 \quad (2)$$

The pseudo-second-order rate constant k, initial sorption rate h, amount of Pb^{2+} adsorbed at equilibrium Q_e obtained from the pseudo second-order model and the linear correlation coefficient R^2 are given in Table-1.

TABLE-1
PSEUDO-SECOND-ORDER RATE CONSTANTS FOR THE ADSORPTION OF Pb(II) AT VARIOUS TEMPERATURE ON TREMOLITE AMIANTHUS

T (ºC)	R^2	Q_e (mg/g)	k (g/(mg min))	h (mg/(g min))
25	0.9760	303.03	0.00038	34.79
35	0.9909	270.27	0.00050	36.76
45	0.9895	263.16	0.00047	32.57
55	0.9878	243.90	0.00051	30.58

Table-1 showed that each pseudo-second-order rate constant for the adsorption of Pb^{2+} at various temperatures increased from 25-55 ºC. This indicates that temperature has only a little effect on Pb^{2+} adsorbed by tremolite amianthus. Increase in temperatures in the range of 25-55 ºC resulted in the increase of the rate constant, k, from 0.00038-0.00051 g/(mg min). In addition, the initial sorption rate h decreased from 34.79-30.58 mg/(g min). The results of the rate constant, k indicated that it's beneficial for Pb^{2+} adsorbed but the results of initial sorption rate, h indicated that it's adverse for Pb^{2+} adsorbed at higher or lower temperature in the range of 25-55 ºC.

Effect of pH: Stock solution of 50 mg/L of the standardized Pb^{2+} was prepared from $Pb(NO_3)_2$. The effect of pH on Pb^{2+} removal was studied at 20 ºC for 1 h as shown in Fig. 4. From Fig. 4, the amount of adsortption increased with increasing pH from 2-6 for Pb^{2+}. At lower pH values, the small amount of Pb^{2+} ions adsorbed is probably due to competitive adsorption of H^+ with metal ions for the exchange site in the system. In addition, structure of tremolite amianthus is unstable. In acid medium, crystal texture of tremolite amianthus is easily destoried and the adsorption capacity is low.

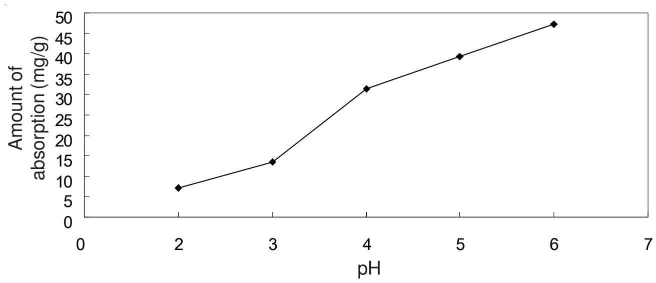


Fig. 4. Effect of pH on adsorption of Pb(II)

Effects of initial concentration and adsorption isotherm: Initial Pb^{2+} concentration whose pH is 6 was adjusted in the ranges of 30-500 mg/L for adsorption on tremolite amianthus at 20-40 ºC for 1 h. The adsorption isotherm for tremolite amianthus was shown in Fig. 5.

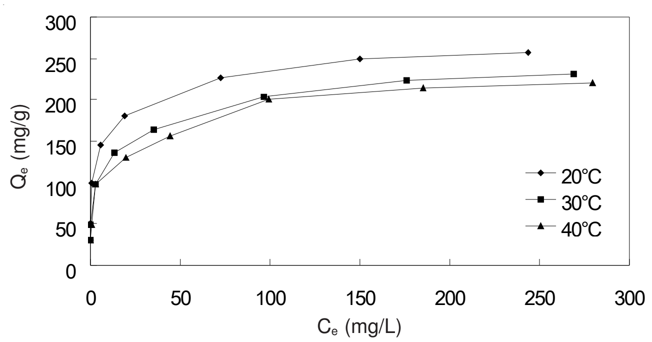


Fig. 5. Adsorption isotherms for treolite amianthus

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherm can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most commonly used[15]. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The model takes the following form:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (3)$$

where Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and Q_0 (mg/g) and K_L (L/mg) are Langmuir constants. Fig. 6 showed the Langmuir plots for tremolite amianthus adsorption.

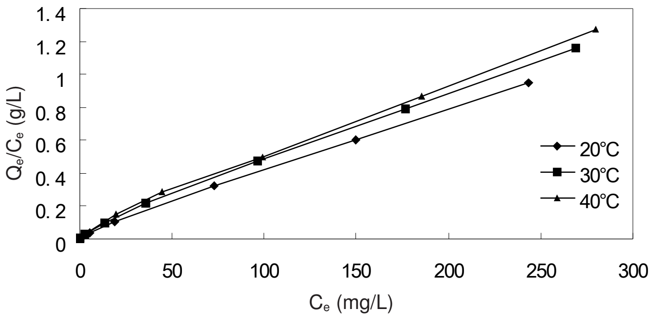


Fig. 6. Langmiur plots for tremolite amianthus adsorption

Based on the further analysis of Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where C_0 (mg/L) is the initial amount of Pb^{2+}. The R_L parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the R_L value: (i) for favourable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$ and (iv) for irreversible adsorption, $R_L = 0$[16].

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

$$\log Q_e = \log K_F = \frac{1}{n} \log C_e \quad (5)$$

where Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_F ($mgL^{1-1/n}L^{1/n}g^{-1}$) and n (g/L) are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

The relative values of Q_0, K_L, K_F and n obtained as calculated from Langmuir and Freundlich models of Pb^{2+} on tremolite amianthus are listed in Tables 2 and 3. Linear plot of Q_e/C_e *versus* C_e was examined to determine Q_0 and K_L values as shown in Tables 2 and 3. At 20, 30, 40 ºC, the Langmuir adsorption maxima Q_0 was quite high with the values of 256.14, 232.56, 222.22 mg/g and the Langmuir equilibrium constant K_L, had a value of 0.281, 0.152, 0.125 for tremolite amianthus. The coefficient of determination of the plot shows that the linear Langmuir equation gives a good fit to the adsorption isotherm for the adsorption of Pb^{2+} onto tremolite amianthus compared with Freundlich equation for the linear plot of log Q_e *versus* log C_e.

Thermodynamic studies: Thermodynamic parameters can be determined by using the equilibrium constant, K_d (Q_e/C_e) which depends on temperature. The change in enthalpy (ΔHº) and entropy (ΔSº) associated to the adsorption process were calculated by using the following equations[17-21]:

TABLE-2
LANGMUIR EQUATION PARAMETERS OF Pb(II) ADSORBED BY TREMOLITE AMIANTHUS

T (°C)	Q_0 (mg/g)	K_L (L/g)	R^2
20	256.14	0.281	0.9983
30	232.56	0.152	0.9967
40	222.22	0.125	0.9960

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (6)$$

where R (8.3145 J/(mol K)) is the ideal gas constant and T (K) is the temperature. The plots of ln K_d against 1/T were shown in Fig. 7. The values of ΔH° and ΔS° of Pb^{2+} adsorption were calculated by fitting the experimental data to eqn. 6 as shown in Fig. 7. The Gibbs free energy, ΔG°, of specific adsorption is calculated from the equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

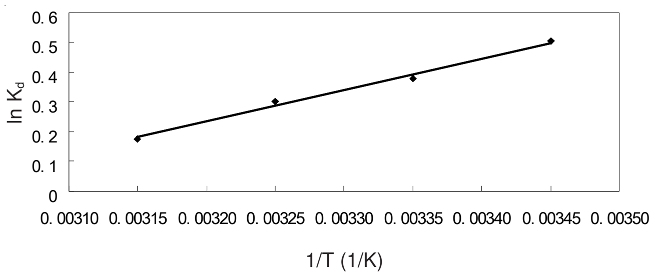


Fig. 7. Relationship between 1/T and ln K_d for tremolite amianthus

The values of ΔH° and ΔS° of Pb^{2+} adsorption were calculated by fitting the experimental data to eqn. 6. ΔG° values were obtained by using eqn. 7.

We took the 150 mg/L of Pb^{2+} solution for the thermodynamic analysis. The thermodynamic parameters for the adsorption of Pb^{2+} were listed in Table-4. From it, the negative value of enthalpy change (ΔH°), indicated that the adsorption of Pb^{2+} on tremolite amianthus was exothermic process. The negative ΔG° values of both Pb^{2+} ions at various temperatures is due to the fact that the adsorption processes are spontaneous and that the negative value of ΔG° increased with an increase in temperature, indicating that the spontaneous nature of adsorption of Pb^{2+} are proportional to the temperature. The negative ΔS° revealed that the orderliness of the adsorbed system was higher than the solution phased before adsorption.

TABLE-3
FREUNDLICH EQUATION PARAMETERS OF Pb(II) ADSORBED BY TREMOLITE AMIANTHUS

T (°C)	K_F ($mg^{1-1/n} L^{1/n} g^{-1}$)	n (g/L)	R^2
20	90.36	4.675	0.9639
30	74.99	4.719	0.9903
40	69.98	4.771	0.9602

Conclusion

In this study, the results obtained from tremolite amianthus used for Pb^{2+} removal from aqueous solution demonstrated to remove Pb^{2+} effectively and tremolite amianthus could be a potential adsorbent to remove Pb^{2+} from real wastewater. The amount of Pb^{2+} adsorbed by tremolite amianthus was high. In addition, the adsorption of Pb^{2+} by tremolite amianthus followed the Langmuir model. The linearity of the plots of the pseudo-second-order model indicated that Pb^{2+} adsorbed by tremolite amianthus was a main chemical reaction rather than physisorption. Furthermore, the negative value of enthalpy change, ΔH° and Gibbs free energy change, ΔG°, indicated that the adsorption of Pb^{2+} onto tremolite amianthus was a feasible, spontaneous thermodynamically and exothermic process.

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