Removal of Lead(II) from Wastewater Using Stishovite Clay

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Abstract: Systematic batch mode studies on adsorption of Pb(II) onto Stishovite clay were carried out as a function of parameters like initial metal concentration, contact time, pH and temperature. The Langmuir and Freundlich adsorption models were applied and the equilibrium data fitted well with both isotherms. The pseudo-second-order kinetic, Elovich, intraparticle diffusion models were tested for the kinetic study. The final results showed that the adsorption process under study could be best described by the pseudo second order equation. Intra particle diffusion studies showed mainly boundary layer effect. Thermodynamic parameters revealed that the adsorption to be spontaneous and endothermic.

Keywords: Stishovite clay, Kinetics, Adsorption isotherm, Thermodynamics of adsorption

Introduction

Lead, one among the heavy metals, is one of the most dangerous contaminant released into the natural waters from various industries such as mining and melting ferrous ores, oil refining, municipal wastes, paint and pigment production and battery manufacturing[1]. When it enters the human body through inhalation or dermal contact, it tends to accumulate in living tissues such as bone, brain, kidney and muscles leading to diseases such as anemia, nephropathy, blood and brain disorders and ultimately even cause death[2-3].

In recent decades, various techniques including chemical coagulation, adsorption, reverse osmosis, electrolysis, ion exchange and membrane seperation[4] *etc*., have been used for reducing the levels of heavy metals in wastewaters. Among these, adsorption technique is mostly preferred for the removal of heavy metals[5-7] because of economic viability, ease of operation and simplicity of the designing. Commercial activated carbon was most widely used as adsorbent. However its high cost and regeneration problems restricted its use. As a result several low-cost adsorptions have been developed by many a researchers all over the globe for the removal of heavy metals from waste waters from the stand point of eco-friendly, effectiveness and economic considerations. Non-conventional adsorbents developed

include clay materials such as kaolinite[8], illite[9], sepiolite[10], montmorillionite[11], siderite, fugirite, magnetite[12], rectorite[13] and vermiculite *etc*. Clay minerals had high sorption, ion-exchange and expansion properties. They were widely used to adsorb all kind of pollutants from large volume of aqueous solutions. The objective of the present study was to explore the feasibility of the removing of Pb(II) from waste waters using Stishovite clay as an adsorbent.
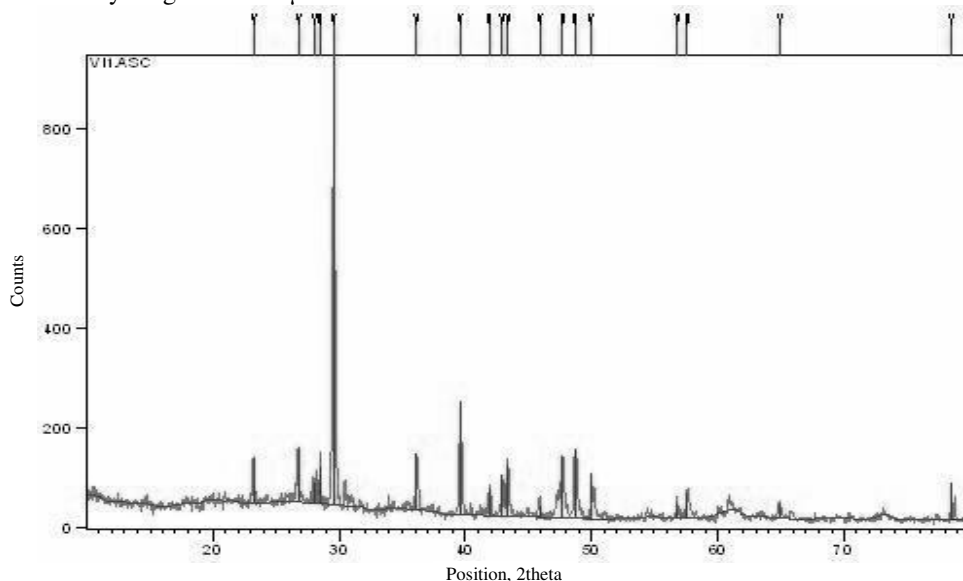
Experimental

A stock solution of (1000 mg/L) lead(II) was prepared by dissolving 1.5985 g of anhydrous lead nitrate in 1000 mL of doubly distilled water.

Determination of lead[14]

Lead(II) was estimated spectrophotometrically using PAR reagent (4-(2-pyridylazo) resorcinol mono sodium salt). A suitable aliquot of the sample containing not more than 50 µg of lead(II) was transferred into a 25 mL volumetric flask. 10 mL of ammonia-ammonium chloride buffer solution (33.8 g NH_4Cl+286 mL of liquid ammonia made up to 500 mL with distilled water) was added to maintain a pH of 10.0 followed by 1 mL of 0.01% solution of PAR reagent. The solution was made up to the mark with distilled water. The absorbance was measured at 520 nm against blank. A calibration graph for (5-50 µg of Pb) was prepared by adapting the above procedure and the concentration of lead(II) in the sample aliquot was calculated by referring the calibration graph.

Characterization of adsorbent

Physicochemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of Stishovite clay (Figure 1) showed characteristic peaks at 30° confirming the presence of Stishovite phase in the clay. The surface morphology of the adsorbents was visualized via scanning electron microscopy (SEM) (Figure 2). The diameter of the clay range was 100 µm.

Figure 1. XRD analysis of Stishovite
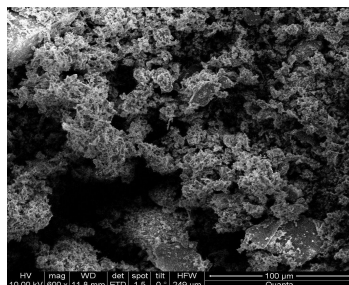
Figure 2. SEM of Stishovite

Batch adsorption experiments

Entire batch mode experiments were carried out by taking 50 mL of the metal solution and a known amount of the adsorbent in a 100 mL conical flask. The flasks were agitated for predetermined time intervals in a thermostat attached with a shaker at the desired temperatures (301 K to 317 K) and then the adsorbent and adsorbate were separated by filtration. Studies on the effects of agitation time, pH, initial metal concentration, adsorbent dose and temperature were carried out by using known amount of adsorbent and 50 mL of metal solution of different concentrations. Metal solution (50 mL) with different amounts of adsorbent was taken to study the effect of adsorbent dosage.

Results and Discussion

Effect of contact time and initial metal concentration

The experimental results of adsorptions at various initial metal concentrations (10, 20, 30 and 40 mg/L) on clay was shown in Figure 3. It was observed that the percentage removal at equilibrium increases from 56.94% to 85.24% as the initial metal concentration was increased from 10 mg/L to 40 mg/L. At lower concentrations, the ratio of the initial number of metal ions to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration.
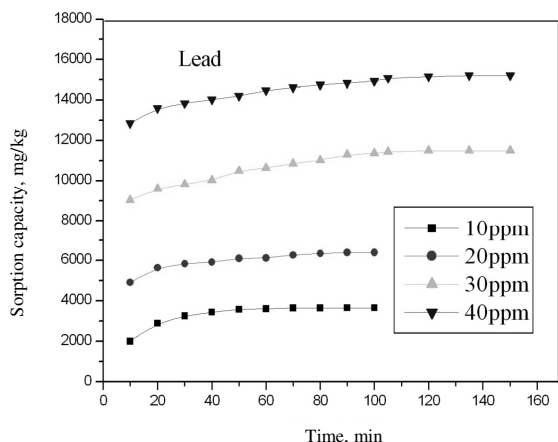

Figure 3. Effect of initial metal concentration

However, at higher concentrations the available sites of adsorption become fewer and hence the percentage removal of metal becomes dependent upon initial concentration[9-10].

The equilibrium was found to get established at 40, 50, 75 and 105 min for lead with the adsorbent as the initial metal concentration was increased from 10 mg/L to 40 mg/L. The curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal on the adsorbent surfaces[15].

Effect of adsorbent dose

The adsorption of the Pb(II) was studied by varying the adsorbent dose (100-1000 mg/50 mL) for 10 to 40 mg/L initial metal concentrations. The percentage of adsorption increased with increase in amount of the adsorbent (Figure 4). This was attributed to increase in surface area and the availability of more adsorption sites[16-17] with increase in the adsorbent dose.
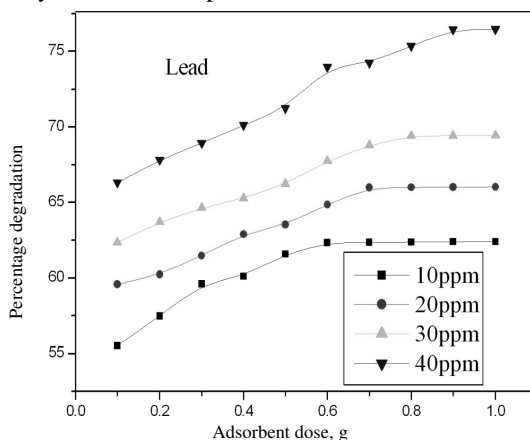
Figure 4. Effect of adsorbent dosage

Effect of pH

Adsorption experiments were carried out at various pH values ranging from 5 to 11, maintaining the pH by adding required amount of dilute hydrochloric acid and sodium hydroxide solutions. The sorption capacity increased with increase in pH. Figure 5 indicates that maximum metal removal had occurred in basic medium.

Effect of temperature

The effect of temperature on the removal of Pb(II) by Sovitetish clay was shown in Figure 6. The amount of metal adsorbed increased with increasing temperature from 301 K to 317 K indicating the adsorption process to be endothermic. This may be due to the increase in the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent with increase in temperature.
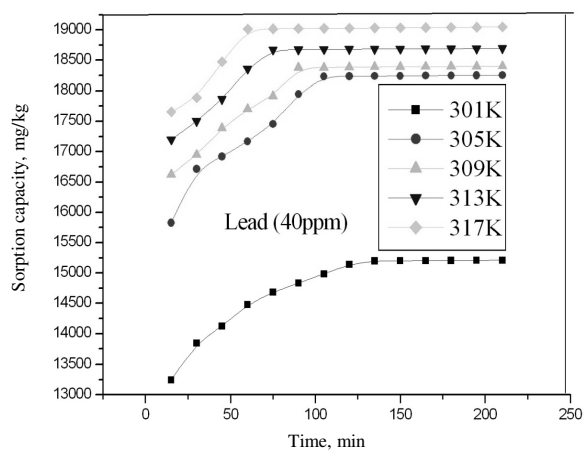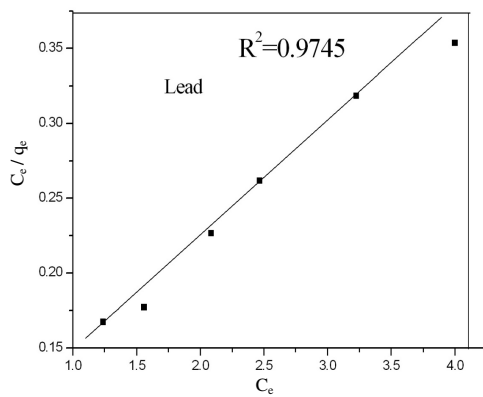
Adsorption isotherms

The experimental data were fit into Langmuir and Freundlich isotherms

Langmuir isotherm

In linear form the Langmuir model[18] is usually expressed as,

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \tag{1}$$

Where C_e is equilibrium concentration of metal (mg/L), q_e is the amount of metal adsorbed at equilibrium (mg/g), 'Q^0' and 'b' are the Langmuir constants correlated to adsorption capacity and rate of adsorption respectively. A linear plot of C_e/q_e *vs.* Ce is shown in Figure 7.
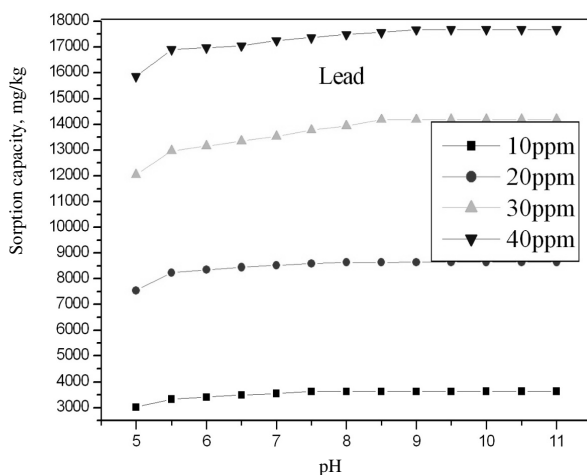
Figure 5. Effect of pH

Figure 6. Effect of temperature

Figure 7. Langmuir isotherm

The values of Q^0 and b were calculated from the slope and intercept of the plots and the values are given in Table 1. These values indicate that the maximum monolayer adsorption capacity of Stishovite clay for Pb(II) was 21.09 mg/g. The crucial features of the Langmuir isotherm was examined by the dimensionless constant separation term (R_L) which was calculated using

$$R_L = \frac{1}{(1 = bC_0)} \tag{2}$$

Where C_0 is initial metal concentration (mg /L). The nature of adsorption is if, $R_L > 1$ Unfavourable, $R_L = 1$ Linear, $R_L = 0$ Irreversible, $0 < R_L < 1$ Favourable. In the present study, the R_L values were all less than unity in the concentration range studied, showing that the adsorption process was favourable.

**Table 1.** Data for Langmuir adsorption isotherm for lead

Conc. of metal, mg/L	Lead (Stishovite clay)			
	R_L	b	Q^0, mg/g	R^2
20	0.181			
40	0.142			
60	0.129	0.265	21.0970	0.9745
80	0.102			
100	0.097			
120	0.0750			

Freundlich isotherm[19]

The Freundlich isotherm can be represented in its logarithmic form as,

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{3}$$

Where K_f and n are Freundlich constants representing adsorption capacity and intensity of the adsorbent respectively. The plot of log q_e *vs.* log C_e shown in Figure 8.
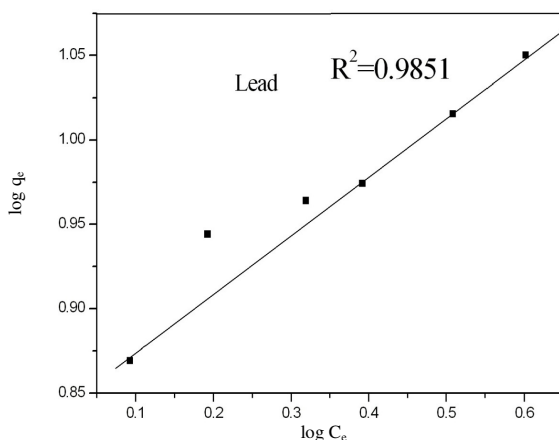
Figure 8. Freundlich isotherm

The linear plot with a regression coefficient of 0.9851 shows that the data for the adsorption of Pb(II) fit well with Freundlich isotherm. The value of n, evaluated as 1.321 indicates that the process was favorable[20]. The value of K_f was found to be 8.091[$mg^{1-1/n}$ $L^{1/n}$ g^{-1}] respectively.

Kinetics of adsorption

In order to investigate the mechanism of adsorption of Pb(II) by the clay the following kinetic models were considered.

Pseudo second order kinetics

In the linearised form pseudo second order kinetic model can be represented as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t.$$
(4)

Where k_2 is the second order rate constant (g.mg^{-1}.min). A plot of t/q_t and t should give a linear relationship if the adsorption follows second order q_e and k_2 can be calculated from the slope and intercept of the plot. The linear plots (Figure 9) obtained from experimental data clearly show that the adsorption process follow pseudo second order kinetics.
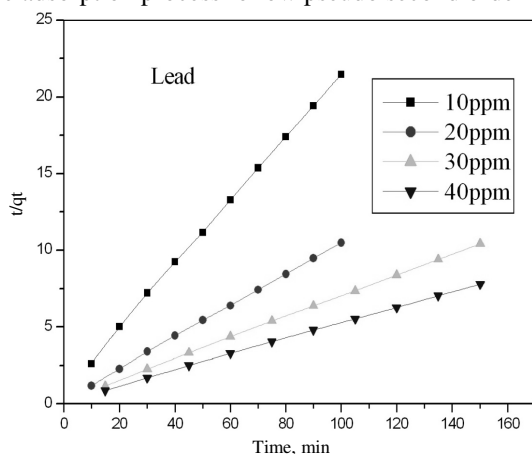

Figure 9. Pseudo second order kinetics

Elovich kinetic model

The Elovich equation mainly applied for chemisorptions and valid for systems with heterogeneous adsorbing surfaces[21] is generally expressed in its integrated form as

$$q_t = \frac{1}{b} \ln t + -\frac{1}{b} \ln(ab)$$
(5)

Where 'a' is the initial adsorption rate (mg.g^{-1}.min) and 'b' is related to the extent of surface coverage and the activation energy for chemisorptions (g.mg^{-1}). A plot of q_t *vs.* ln t gives a straight line with a slope of 1/b and an intercept log 1/b ln (ab) with good correlation coefficients (0.8977, 0.9174, 0.9386 and 0.9586). Figure 10 strongly supports the validity of the Elovich equation suggesting chemisorptions.

Thermodynamic of adsorption

Thermodynamic parameters like ΔH^0, ΔS^0 and ΔG^0 were evaluated using the following equations

$$\ln Kc = \Delta S^0/R - \Delta H^0/R$$
(6)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
(7)

Where K_C is the Langmuir equilibrium constant, ΔH^0, ΔS^0 and ΔG^0, are the standard enthalpy, entropy and free energy change of adsorption respectively. Negative free energy

changes (1.149, 1.164, 1.179, 1.193, 1.208 kJ/mol at 301 K - 317 K) and positive entropy change (3.7155 kJ/mol) of adsorption indicate that the adsorption is favorable and spontaneous process. The endothermic nature of adsorption is confirmed by the positive value of ΔH^0 (30.9629 kJ/mol).
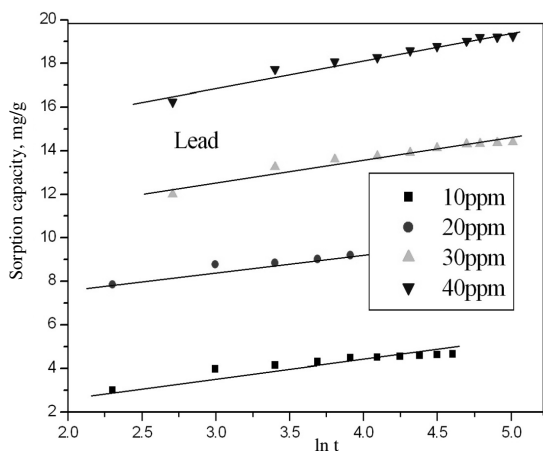

Figure 10. Elovich kinetic model

Desorption studies

Desorption studies with acetic acid revealed that the regeneration of adsorbent was not satisfactory, which confirms the chemisorptive nature of adsorption.

Conclusion

The present investigation showed that Stishovite clay can be used as an effective adsorbent for removal of lead(II). The amount of metal adsorbed varied with initial metal concentration, adsorbent dose, pH and temperature. Removal of metal by Stishovite clay obeyed both Langmuir and Freundlich isotherms. The adsorption process followed pseudo second order kinetics.

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