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Kinetic and Thermodynamic Studies on Biosorption of Lead ions by Chemically Modified Sawdust

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ABSTRACT

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. One of the most important environmental problems is water resources pollution by heavymetals. Biosorption is affordable adsorbents for the removal of heavy metals from aqueous solutions. This study explores the adsorption potential of Pb(II) by acid modified sawdust in aqueous solution. The influences of several main parameters such as pH and adsorbent dosage were studied. The adsorption kinetics were analyzed by pseudo first order and pseudo second order kinetic models. Thermodynamic parameters including changes of free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) during the biosorption were determined.

Keywords: Biosorption, Pb(II), Sawdust, Kinetic Models, Thermodynamic Parameters

I. INTRODUCTION

Water pollution by heavy metals has received wide spread attention for many decades and has been a major cause of concern due to generation of a high toxicological risk for human health, ecosystem and agriculture. Most of heavy metals are toxic and due to their non-biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders. Exposure of lead can cause anemia, diseases of the liver and kidneys, brain damage and ultimately death. Besides chronic exposure to these contaminants present even at low concentrations in the environment can prove to be harmful to the human health. For these reasons, heavy metals must be removed as much as possible from industrial effluents. Several methods have been proposed for the removal of heavy metals as ion exchange, chemical precipitation and electrochemical treatment [1,2,3]. Most methods to remove metal ions from solution are expensive, so the use of cheap agricultural wastes such as natural leaves [4], grape stalk wastes [5], tea waste [6], maize leaf [7], watermelon shell [8] and papaya peel [9] as adsorbents have been highlighted for metal removal from wastewater. This paper presents the study of biosorption characteristics of acid modified sawdust (SDA) for the removal of Pb(II) ions from aqueous solutions.

II. MATERIALS AND METHODS

A. Preparation of Adsorbent

The sawdust was collected from a local saw mill then they were ground using a mechanical grinder, and the resultant powder was sieved in a 150 mm particle sized mesh. They were thoroughly washed with distilled water to remove dust, mud and other impurities and were heated in an oven at 80^oC for 2 hours. About 10 g of oven dried sawdust were poured into 250 ml flask containing 100 ml of 0.1 M HCl solution, and then were shaken at 200 rpm for 4 hours at room temperature. The mixture was left over night, and then was washed several times with distilled water to provide neutral pH. The adsorbent was then oven dried at 85^oC for 2 hours. Finally, acid modified sawdust (SDA) was separated and stored in plastic container for further experiments.

B. Preparation of stock solution

Stock solution of lead was prepared by disssolving lead acetate in deionized water. All working solutions of varying concentrations were obtained by diluting the stock solution with deionized water. The pH of the effluent was adjusted by using 0.2 M acetic acid and 0.2 M sodium acetate solutions. The concentration of metal ions in effluent was analyzed by atomic absorption spectrophotometer (AAS).

C. Biosorption Experiments

Biosorption experiments were carried out by shaking a stopper flask containing 25 ml of 100 mg/L metal ion solution and 0.2 g of adsorbent at 200 rpm for 60 min. The sample was allowed to settle and then it was filtered through a Whatmann filter paper. The filtrate of the sample was analyzed in an AAS for the final concentration of metal ions in aqueous solution. The amount of metal adsorbed per unit mass of the adsorbent was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{M} \qquad ....(1)$$

where, q is the metal uptake (mg/g), C_i and C_f are the initial and final or equilibrium metal concentration inthe solution (mg/L), V is the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g). The percentage removal (%R) of metal ions was calculated from the following equation:

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100 \qquad ....(2)$$

III. RESULTS AND DISCUSSION

A. Effect of pH

The percentage removal of Pb(II) ions was studied, using SBA as adsorbent in the pH range of 3 to 6. The experimental results are shown in fig 1. The percentage removal of Pb(II) ions investigated was found to increase with an increase in the solution pH upto 5, and then it decreased with the increase in the solution pH. At a lower pH, the surface of the adsorbent was surrounded by H^+ ions. The adsorbent surface becomes more positively charged, so that the attraction between the adsorbent and metal ions get reduced. As the pH increases, the adsorbent surface becomes less positively charged and this facilitates higher metal ion removal. The percentage removal of Pb(II) by SDA increased from 34.72% to 52.00% when the pH of the solution was increased from 3 to 5.

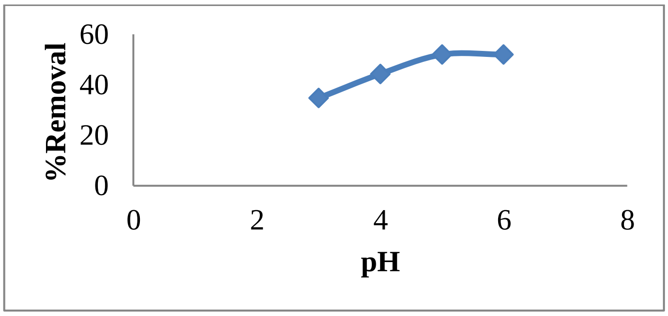

Figure 1: Effect of pH on the biosorption of Pb(II) by SDA

B. Effect of adsorbent dosage

The percentage removal of Pb(II) ions against adsorbent dosage were plotted and shown in fig 2. It is evident from the plot that the percentage removal of metal ions from the aqueous solution increases with the increase in the adsorbent dosage. Such behavior is obvious because the number of active sites available for metal ion removal would be more as the amount of the adsorbent increases. The percentage removal of Pb(II) by SDA increased from 40.48% to 52.00% when the adsorbent dosage was increased from 0.1 to 0.5 g.

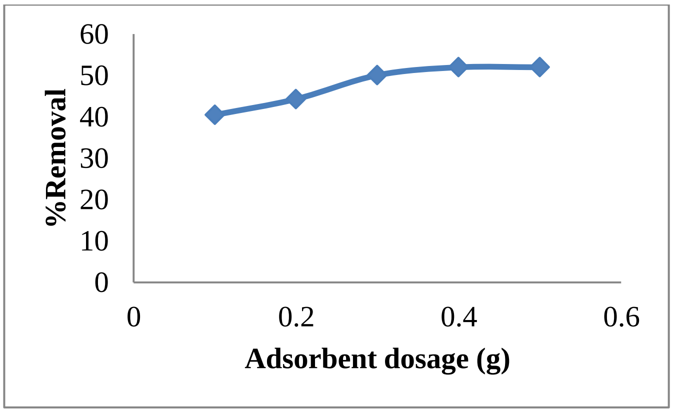

Figure 2: Effect of adsorbent dosage on the biosorption of Pb(II) by SDA

C. Kinetic Studies

Parameters from two kinetic models, pseudo first order and pseudo second order, were used to examine the biosorption kinetics of Pb(II) ions uptake onto SDA.

Kinetic studies were carried out at different contact time ranging from 10 to 120 min.

Pseudo first order kinetic model

The pseudo first order equation is generally expressed as follows [10]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad \text{.................(3)}$$

After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (3) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad \text{.................(4)}$$

where q_e and q_t are the amount of metal ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium and at time t respectively, k_1 is the rate constant of the pseudo first order adsorption process (min^{-1}) and t is the contact time (min). The q_e and k_1 were calculated from the plot of $\log(q_e-q_t)$ against t, and are shown in fig 3.

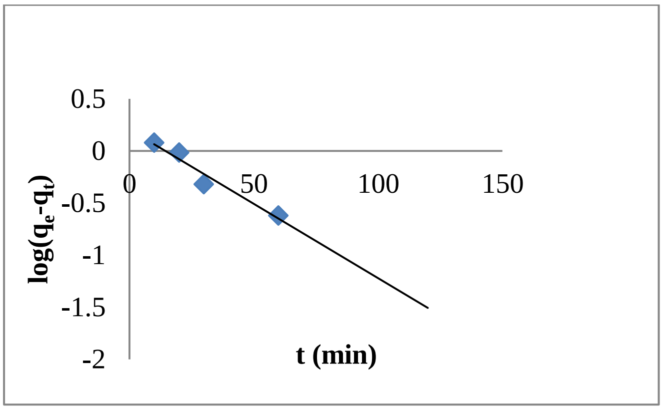

Figure 3 : Pseudo first order kinetic plot for the biosorption of Pb(II) by SDA

Pseudo second order kinetic model

The pseudo second order equation is expressed as follows [11]:

$$dq/dt = k_2(q_e - q_t)^2 \quad \text{...............(5)}$$

For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t the integrated form of equation (5) becomes

$$t/q_t = 1/k_2 q_e^2 + t/q_t \quad \text{...............(6)}$$

where k_2 is the pseudo second order rate constant (g $mg^{-1}min^{-1}$). The q_e and k_2 were obtained by linear plot of t/q_t versus t, and are shown in fig 4. The values of k_1, k_2, R^2, experimental and the calculated q_e are listed in table 1. The pseudo first order was not satisfactory to explain the experimental data, whereas the calculated, $q_{e\ cal}$ values derived from the pseudo second order model for the sorption of metal ions were very close to the experimental ($q_{e\ exp}$) values. From the R^2 values the second order equation appeared to be better fitting model than first order because it has higher R^2 value. The higher values confirm that the adsorption data are well represented by pseudo second order kinetics.

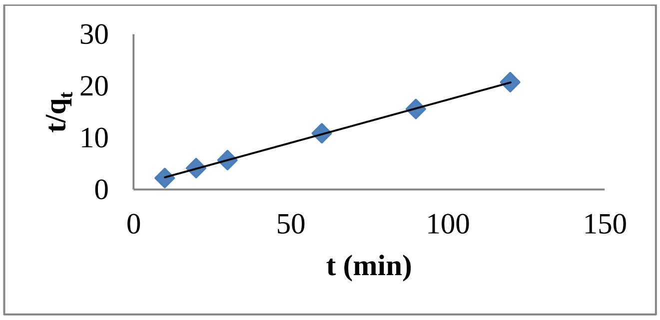

Figure 4: Pseudo second order kinetic plot for the biosorption of Pb(II) by SDA

Table 1: Pseudo first order and second order kinetic parameters of Pb(II) biosorption by SDA

Pseudo first order kinetic model				Pseudo second order kinetic model		
$q_{e\ exp}$ (mg/g)	k_1	$q_{e\ cal}$(mg/g)	R^2	k_2	$q_{e\ cal}$(mg/g)	R^2
5.780	0.0322	1.6180	0.952	0.0421	5.9880	0.999

D. Thermodynamic studies

Biosorption experiments were conducted at different temperatures (313 K, 323 K and 333 K) to find the thermodynamic parameters including the changes in free energy ΔG (KJ/mol), enthalpy ΔH (KJ/mol) and entropy ΔS (KJ/mol/K), in order to illustrate the thermodynamic behavior of adsorption process. Thermodynamic parameters of adsorption can be evaluated from the following equations [12]

$$K_c = \frac{q_e}{C_e} \qquad \text{...............(7)}$$

$$\Delta G = -RT\ln Kc \qquad \text{...............(8)}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{...............(9)}$$

where Kc is the equilibrium constant, Ce is the equilibrium concentration in solution (mg/L) and q_e is the amount of metal ions adsorbed per unit mass of the adsorbent (mg/g), R is the gas constant (8.314 J/mol K) and T is the temperature (K). The values of ΔH and ΔS were determined from the slope and the intercept from the plot of ΔG versus T (fig 5). The thermodynamic parameters are listed in table 2. The ΔG values are found to be negative which indicate that the adsorption process is spontaneous. The positive values of ΔH showed the endothermic nature of adsorption and it governs the possibility of physical adsorption.

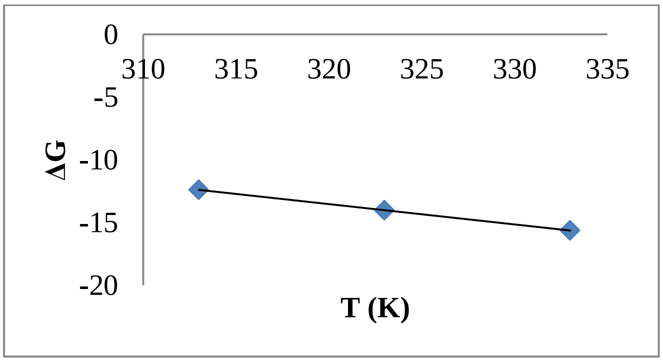

Figure 5: Thermodynamic plot for the biosorption of Pb(II) by SDA

TABLE 2: Thermodynamic parameters of Pb(II) biosorption by SDA

-ΔG (KJ/mol)			ΔH (KJ/mol /K)	ΔS (KJ/mol /K)	R^2
313 K	323 K	333 K			
12.3730	14.0191	15.6190	38.41	0.162	0.999

IV. CONCLUSION

The experimental investigation concluded that SDA could be used as potential biosorbent for removal of Pb(II) ions from aqueous solutions. The percentage removal of Pb(II) ions in aqueous solution increased with increase in the pH and adsorbent dosage. The kinetic studies revealed that the biosorption process followed the pseudo second order kinetic model. Thermodynamic parameters ΔG, ΔH and ΔS showed the endothermic and spontaneous nature of the biosorption of Pb(II) ions onto SDA.

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