Enthalpy and Entropy Changes of Chitosan-Coated onto Pineapple-Waste for Lead Adsorption

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Abstract - The enthalpy (∆H°) and entropy (∆S°) were obtained from the Van’t Hoff equation by using the chitosan-coated onto pineapple-waste as the effective adsorbent for the lead adsorption. The chitosan-coated onto pineapple-waste had been characterized by scanning electron microscopy (SEM). The specific surface area (BET) of chitosan-coated onto pineapple-waste was 70 m²/g. The effects of pH, initial lead concentration, time and temperature on the adsorption were studied. The optimum pH value for adsorption onto adsorbents was 6.0. The equilibrium data could be described well by the Langmuir isotherm equation. A separation factor was used to consider the favorable adsorption. The enthalpy (∆H°) and entropy changes (∆S°) of chitosan-coated onto pineapple waste were 3,556.1 J/mol and 25.745 J/mol K, respectively.

Keywords: pineapple-waste, chitosan, lead adsorption, enthalpy, entropy

Introduction

The hazards of human life from the effects of various metal ions were received extensive attention in the past 30 years. The effects of lead on neurobehavioral development [1] and brain cell function [2] were investigated. The accumulation of lead in river beds [3] was detected and given cause for concern. Consequently, methods to remove lead from wastewaters and drinking waters were subjected of several research works [4-6]. Adsorption is an effective separation process for a wide variety of applications. It is now recognized as an effective and economic method for the removal of pollutants from wastewaters. The most widely used adsorbent was activated carbon but in the past 10 years considerable attention was directed towards low cost biosorbents because activated carbon is expensive and an alternative inexpensive adsorbent could drastically reduce the cost of an adsorption system [7]. Many wastes or naturally occurring materials were investigated to assess their suitability for application in the field of water pollution control. The use of low-cost natural materials for the removal of lead includes fly ash, peat, and waste sludges [8-11], the pineapple-waste, chitosan, and chitosan-coated onto pineapple-waste, as adsorbents were used to remove lead by adsorption. The enthalpy (∆H°) and entropy (∆S°) that might affect the adsorption including pH, lead concentration temperatures and types of adsorbents were also investigated.

Material

Pineapple-waste was obtained from the solid waste of filtration process in the pineapple juice manufacturing located in Prachuabkiriikhi (Southern of Thailand). The pineapple-waste was washed with distilled water to remove easily suspension materials many times and dried in oven at 105 °C for 48 h. The dried waste was sieved into particle size of 50-100 mesh and kept in desiccator. The structure of pineapple-waste is shown as Fig. 1.

Fig. 1 Structure of cellulose

Chitosan is a biopolymer found in body of shellfish, crustaceans and some fungi. The free amino group of this biopolymer is shown different properties such as anti-microbial, anti-acid and chelating of metal ions. Chitosan was used as an adsorbent for the removal of the metal ions from many industrial applications [12]. Chitosan is a partially deacetylated polymer of acetylglucosamine and it is usually prepared from chitin. The structure of chitosan is shown in Fig 2. Commercial chitosan was purchased from Nateenumchok Chitosan company. Then it was sieved into particle size of 50-100
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mesh. For removing the impurity of chitosan was poured in distilled waster and boiled for 30 min. Then it was washed several times with distilled water and dried in oven at 105 °C for 48 h. and kept in desiccator.

Chitosan-coated onto pineapple-waste was prepared with spraying the chitosan solution at concentration of 0.5 % V/V chitosan in 2% V/V acetic acid on 50 g to 100 g. Then it was dried in oven at 70 °C for 48 h and kept in desiccator.

All chemical used in the experiments were analytical grade and distilled water was used to prepare solutions. Lead solution was prepared by dissolving from lead nitrate (Pb(NO₃)₂) from Aldrich Chemical in water.

**Experimental**

The batch adsorption experiments were performed to determine the adsorption characteristics of lead on adsorbent. Isotherm adsorption tests were conducted in a series of 250 ml glass flask. Each test flask was filled with 100 ml of lead solution of varying concentrations and adjusted to desired time, temperature and pH with either nitric acid or sodium hydroxide solution. A known concentration of adsorbent was filled into each test flask and mixed in the shaking water bath with controlled temperature at constant speed of 110 rpm. The time required to reach adsorption equilibrium, about 2 h, was determined thermodynamic properties. Samples were withdrawn after 2 h reaction time, filtered through 0.45 µm membrane filter, and then analyzed with an atomic adsorption spectrophotometer (Varian model SpectrAA-300).

The enthalpy and entropy change experiments were carried out with a special parameter for lead nitrate concentration (100, 150, 200 and 250 ppm), at pH 6, 30 °C, adsorbent 5 g/L and particle size 50-100 mesh, temperature (30, 40 and 50 °C), pH 6, lead concentration 100 ppm, adsorbent 5 g/L and particle size 50-100 mesh. The apparatus used in the thermodynamic experiments were similar to those used in the batch experiments.

**Results and Discussion**

The specific surface area (BET) of pineapple-waste, chitosan, and chitosan-coated onto pineapple-waste measured by Micromeritic Chemisorb 2750 automated system were 45, 60 and 70 m²/g, respectively. Scanning electron micrographs (SEM) of adsorbents (pineapple-waste, chitosan, and chitosancoated onto pineapple-waste) at magnification 500x are shown in Figs. 3-5.

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serve as coordination and electrostatic interaction mechanism can be expressed as

\[ R\text{-OH} + \text{Pb}^{2+} \rightleftharpoons R\text{-O-Pb}^{+} + \text{H}^+ \]  \hspace{1cm} (1)

\[ R\text{-NH}_2 + \text{Pb}^{2+} \rightleftharpoons \text{Pb}(R\text{-NH}_2)^+ + \text{H}^+ \]  \hspace{1cm} (2)

From the equilibrium studies, the lead adsorption efficiency as a function of pH was examined over a pH range of 3-8. Fig. 6 shows the lead removal efficiency as a function pH. At pH below 6.0, the removal efficiency of lead descends abruptly, whereas the removal increases in the range from 5.0-6.0. As shown in equations (1-2) increasing pH favors the attractive electrostatic force from R-OH functional group, enhancing the adsorption of cationic lead species.

These studies showed that chitosan could be used as a adsorbent, since its amino and hydroxyl groups can act as chelating sites. The removal of lead from pineapple-waste was higher than that of chitosan since it had more surface area. And also the removal of lead from chitosan-coated onto pineapple-waste was higher than that of pineapple-waste with the same result about the higher surface area.

The adsorption data at equilibrium for a wide range of adsorbate concentrations were well described by various models of adsorption isotherm, such as the Langmuir and Freundlich models [13]. The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and those sites are equal, resulting in equal energies and enthalpies of adsorption. The strength of the intermolecular attractive forces is believed to fall of rapidly with distance. The equation for Langmuir isotherm is as follows:

\[ q_e = \frac{a_l K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (3)

Linear form this equation is:

\[ \frac{1}{q_e} = \frac{1}{a_l} + \frac{1}{a_l K_L C_e} \]  \hspace{1cm} (4)

Where \( q_e \) is lead concentration on adsorbent at equilibrium time (mg/g), \( C_e \) is the lead concentration on solution at equilibrium (ppm), and \( a_l \) and \( K_L \) are the Langmuir coefficients related to adsorption capacity and energy of adsorption, respectively. Langmuir coefficients \( (a_l \) and \( K_L) \) can be calculated from the slope and intercept from equation (4). Webi and Chakravort [14] proposed that the Langmuir constant, \( K_L \), could be expressed in term of a dimensionless constant, separation factor (SF), which is defined by

\[ SF = \frac{1}{1 + K_L C_0} \]  \hspace{1cm} (5)

Where \( K_L \) was the Langmuir constant and \( C_0 \) (ppm) was the initial concentration of the adsorbate. The smaller SF value indicates a highly favorable adsorption.

Freundlich isotherm predicts that the lead concentration on the adsorbent will increase as long as there is an increase of concentration in liquid. Such as isotherm is another form of Langmuir isotherm which was stated for amorphous surface. The amount adsorbed is summation of the adsorption of all sites, each having bond energy. Equation of Freundlich isotherm is as follows [13]:

\[ q_e = K_F C_e^{1/n_F} \]  \hspace{1cm} (6)

\( K_F \) is the Freundlich constant and gives the capacity of the adsorbent and \( n_F \) is the Freundlich exponent and presents an indication of the favorability [15]. Linear form this equation is as follows:

\[ \ln q_e = \ln K_F - \frac{1}{n_F} \ln C_e \]  \hspace{1cm} (7)

The separation factor (SF), which is defined by

\[ SF = \frac{1}{1 + K_F C_0} \]  \hspace{1cm} (8)

Where \( K_F \) is the Freundlich constant. The Langmuir and Freundlich isotherms for lead adsorption on different adsorbents 5 g/L at 30 °C and pH 6 are shown in Figs. 7-8. The calculated \( a_l, K_L, SF \) and correlation coefficients (\( R^2 \)) for Langmuir equation and \( K_F, n_F \) and \( R^2 \) for the Freundlich equation at different reaction temperatures, lead concentration 100 ppm, pH 6 and adsorbent 5 g/L are listed in Tables 1 and 2. The Langmuir constants \( a_l \) and \( K_L \) increase with increased temperatures, showing the adsorption process to be endothermic reaction. The values of the separation
factor (SF) are far smaller than 1 and decrease with increases in temperatures, which indicates high adsorption for high reaction temperatures. The capacity of waste \( K_F \) and the intensity of adsorption \( 1/n_F \) also reflect the same trend. Effect of types of adsorbent on the adsorption isotherm coefficients of Langmuir and Freundlich are listed in Tables 1 and 2. It shows that the adsorption capacity is considerably influenced by the types of adsorbent. The constants \( a_L, K_L, \) and \( K_F \) increase but \( n_F \) decrease \((1/n_F \) increase) with increase in surface area of adsorbent. The amount of surface area of chitosan is lower than those of pineapple-waste and chitosan-coated onto pineapple-waste, respectively. The separation factor decreases with the amount of surface area. These would imply that the amount of surface area of adsorbent could increase the uptake capacity at equilibrium.

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Thus the correlation of equilibrium data by either theoretical or empirical equations is essential for practical design and operation of adsorption system. Two equilibrium isotherms including Langmuir and Freundlich of lead on three types of adsorbent have been tested as shown in Tables 1 and 2. The correlation coefficients \( R^2 \) for all adsorbents of Langmuir isotherm are higher than those of Freundlich isotherm indicating that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on adsorbents surface.

The enthalpy \( \Delta H^\circ \) and entropy \( \Delta S^\circ \) are calculated using the equations as follows:

\[
\Delta G^\circ = -RT \ln K
\]

\[
\frac{\Delta G^\circ}{T} = \frac{\Delta H^\circ}{T} - \Delta S^\circ
\]

where \( R \) is the universal gas constant \( (8.314 \text{ kJ/kmol K}) \), \( T \) is temperature in kelvin \( (K) \) and \( K_L \) is the Langmuir adsorption constant that can obtained from the equilibrium study. The enthalpy \( \Delta H^\circ \) and entropy \( \Delta S^\circ \) can be obtained from the slope and intercept of Van’t Hoff from equation (10). \( K \) is the ratio of
equilibrium lead concentration \( C_e \) on adsorbent and the lead concentration on solution at equilibrium \( C_v \).

The enthalpy (\( \Delta H^\circ \)) and entropy (\( \Delta S^\circ \)) can be obtained from the slope and intercept of Van’t Hoff from equation (10) as shown in Fig.9. The calculated parameter constants at lead concentration 100 ppm, pH 6 and adsorbent 5 g/L are listed in Table 3.

The values of entropy changes (\( \Delta S^\circ \)) can be found 29.283 J/mol K for pineapple-waste, 29.087 J/mol K for chitosan and 25.745 J/mol K for chitosan-coated onto pineapple-waste. The positive values of the entropy changes (\( \Delta S^\circ \)) show the higher randomness tendency at the absorbents/adsorbates interface during the lead adsorption indicating the entropy changes (\( \Delta S^\circ \)) of pineapple-waste is higher than those of chitosan and chitosan-coated onto pineapple-waste, respectively. The negative \( \Delta G^\circ \) value and positive \( \Delta H^\circ \) and \( \Delta S^\circ \) values give a spontaneous process at high temperatures. The result is similar to other works [17-19].

**Conclusion**

Chitosan-coated onto pineapple-waste can be used as an effective adsorbent and higher surface area for lead adsorption. The Langmuir equation is the better than fit equilibrium isotherm from Freundlich isotherm for the sorption of lead onto chitosan, pineapple-waste and chitosan-coated onto pineapple-waste based on a linearized correlation coefficient. The enthalpy (\( \Delta H^\circ \)) and entropy changes (\( \Delta S^\circ \)) of chitosan-coated onto pineapple-waste are 3.5561 kJ/mol and 36.58 J/mol K, respectively.

**References**


