Equilibrium Isotherm, Thermodynamic and Kinetic Studies of Lead adsorption onto pineapple and paper waste sludges

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***Abstract*—**The adsorptions of lead from aqueous solution by pineapple and paper waste sludges are studied through equilibrium isotherm. Langmuir and Freundlich adsorption models are applied in order to describe the Langmuir coefficient (a_L), Langmuir constant (K_L), separation factor (*SF*), Freundlich constant (K_F), intensity of Fruendlich adsorption (n_F^{-1}). The Gibb free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) are calculated for thermodynamic parameters. The adsorption of rate constant (k_{ad}) are determined with from kinetics studies; zero-order, first-order, and second-order adsorption. The activation energy (E_a) of adsorption is applied with Arrhenius equation. Langmuir adsorption model presents better fit with experimental data. The k_{ad} from first- and second-order adsorption have the high correlation coefficient (R^2) with concentration 100-250 ppm, temperature 30-50 °C, and pH 6.

***Keywords*—**Equilibrium isotherm, Thermodynamic, Kinetic, Lead adsorption.

INTRODUCTION

Many industries, especially plating facilities and electronic manufacturing often lead to the containing of heavy metals in the effluent of wastewater which is the serious environmental problems. All heavy metals are toxic and non-biodegradable and should be separated from wastewater. There are several ways for separation heavy metals from wastewater such as chemical separation, filtration, membrane separation, electrochemical treatment, ion exchange, and adsorption [1-5]. All these methods, with the exception of adsorption are costly, have low output and are incapable of removing trace level of heavy metals from wastewater. Adsorption has been shown to be a feasible alternative method for removing heavy metals from wastewater. Several natural and synthetic hydrous solids have been investigated as adsorbent of heavy metals. Among these, metal oxides [6-8] and activated carbon [9-10] are the most extensively employed, but the high cost of these materials limits their large-scale use for removal of metals [11]. Adsorbents can be used for water and wastewater treatment and indeed they are widely used due to their higher output and low costs [12-16]. Among current adsorbents, activated carbon is used in different industries, but it is not a selective adsorbent. Recently, a number of studies were carried out on low cost adsorbents from natural resources. The use of low cost adsorbent for heavy metals derived from natural resources has been reviewed by Baily, Olin, Bricka, and Adrian [17] and Babel and Kurniawan [18]. Such the low cost adsorbents are pineapple and paper waste sludges which are the biodegradable.

Lead (Pb) is a highly toxic metal that is very poisonous for neurobehavioral development [19] and brain cell function [20] even in trace concentration (ppm) and therefore, before the disposal of lead containing industrial wastes their lead content should be eliminated. Many researches were published on removing of lead ions by different adsorbents such as natural and industrial materials, granular activated carbon, char, and chitosan. [21-23] In the present research, the pineapple and paper waste sludges as adsorbents to remove lead from wastewater treatment, the equilibrium and kinetic sorptions and thermodynamic studies have been studied.

MATERIAL

Types of adsorbent

Pineapple waste sludge was obtained from the solid waste of filtration process in the pineapple juice manufacturing located in Prajuabkirikhun (southern of Thailand). Paper waste sludge was obtained from the final recycle paper process of the paper processing factory located in Samutpragran (Thailand). The pineapple and paper waste sludges were washed with distilled water to remove easily suspension materials many times and dried in oven at 105 °C for 48 h. The dried sludges were sieved into particle size of 2 mm and kept in desiccator. The structures of pineapple and paper waste sludges are the cellulose as shown in Fig. 1.

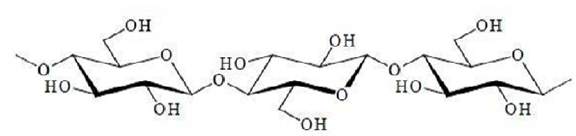

Fig. 1 Cellulose structure of pineapple and paper waste sludges

The specific surface area (BET) of pineapple and paper waste sludges measured by Micromeritic Chemisorb 2750 automated system are 45×10^2 $cm^2 \cdot g^{-1}$, and 205×10^2 $cm^2 \cdot g^{-1}$, respectively.

Scanning electron micrographs (SEM) of pineapple and paper waste sludges at magnification 500 μm are shown in Figs. 2-3. The functional group of materials is hydroxyl (R-OH) group, which can serve as coordination and electrostatic interaction sites to adsorb heavy metals. The adsorption mechanism can be expressed as

$$R\text{-}OH + Pb^{2+} \rightleftharpoons R\text{-}O\text{-}Pb^{+} + H^{+} \qquad (1)$$

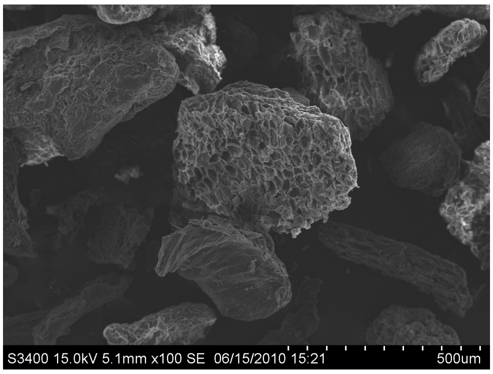

Fig. 2 SEM micrograph of pineapple waste sludge at magnification 500 µm

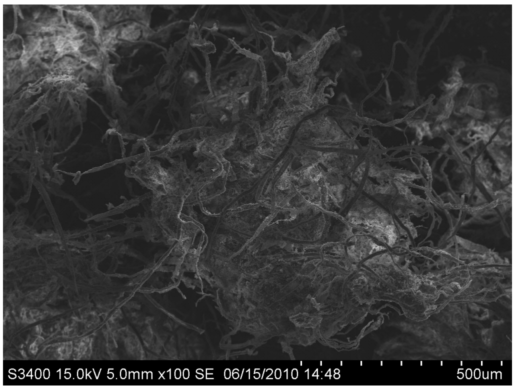

Fig. 3 SEM micrograph of paper waste sludge at magnification 500 µm

All chemical used in the experiments were analytical grade and distilled water was used to prepared solutions. Lead solution was prepared by dissolving from lead nitrate ($Pb(NO_3)_2$) from Aldrich Chemical in water.

RESULT AND DISCUSSION

Equilibrium Isotherm

From the equilibrium isotherm, the lead adsorption efficiency as a function of pH was examined over a pH range of 2-8. Fig. 4 shows the lead removal efficiency as a function pH. At pH below 6.0, the removal efficiency of lead onto paper waste sludge descends abruptly, whereas the removal increases in the range from 5.0-6.0. As shown in (1) increasing pH favors the attractive electrostatic force from R-OH functional group, enhancing the adsorption of cationic lead species.

These studies show that pineapple waste sludge can be used as a adsorbent, since its hydroxyl groups can act as chelating sites. The removal of lead from pineapple waste sludge is lower than that of paper waste sludge since it has less surface area.

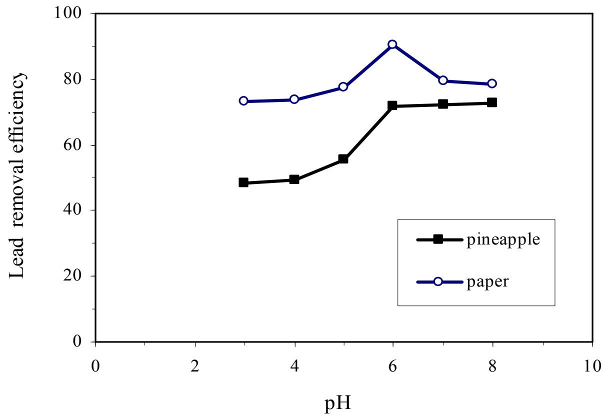

Fig. 4 Lead removal efficiency by pineapple and paper waste sludges 5 $g \cdot L^{-1}$ with different pH at lead concentration 100 ppm, and temperature 30 °C

The adsorption data at equilibrium for a wide range of adsorbate concentrations are well described by various models of adsorption isotherm, such as the Langmuir and Freundlich models [24]. 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:

$$q_e = \frac{a_L K_L C_e}{1 + K_L C_e} \tag{2}$$

Linear form this equation is:

$$\frac{1}{q_e} = \frac{1}{a_L} + \frac{1}{a_L K_L C_e} \tag{3}$$

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 (3). Webi and Chakravort [25] propose that the Langmuir constant, K_L, can be expressed in term of a dimensionless constant, separation factor (*SF*), which is defined by

$$SF = \frac{1}{1 + K_L C_0} \tag{4}$$

Where K_L is the Langmuir constant and C_0 (ppm) is 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 [24]:

$$q_e = K_F C_e^{1/n_F} \quad (5)$$

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 [26]. Linear form this equation is as follows:

$$\log q_e = \log K_F - \frac{1}{n_F} \log C_e \quad (6)$$

The separation factor (*SF*), which is defined by

$$SF = \frac{1}{1 + K_F C_0} \quad (7)$$

where K_F is the Freundlich constant. The Langmuir isotherms for lead adsorption on pineapple and paper waste sludges 5 g·L^{-1} at pH 6, and different temperatures are shown in Figs.5-7. The Freundlich isotherms for lead adsorption on different adsorbents 5 g·L^{-1} at pH 6, and different temperatures are shown in Figs. 8-10. 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 temperatures, lead concentration 100 ppm, pH 6 and adsorbent 5 g·L^{-1} 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 sludge (K_F) and the intensity of adsorption (n_F^{-1}) 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 and n_F^{-1} increase with increase in adsorbent surface area. The amount of surface area of pineapple is lower than those of paper waste sludge. 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.

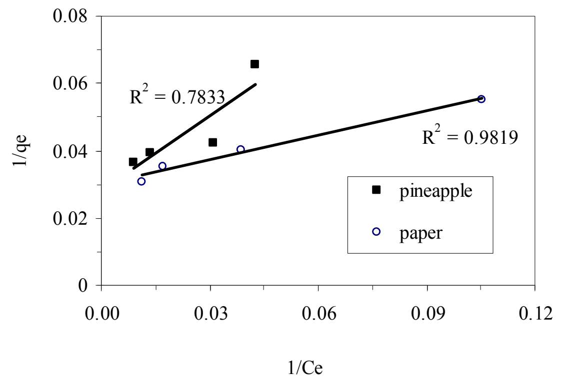

Fig. 5 Langmuir isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 30 °C and pH 6

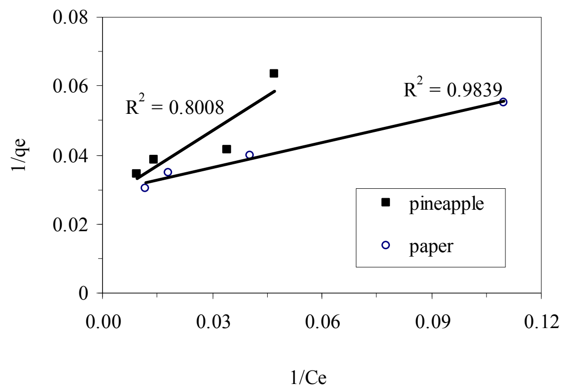

Fig. 6 Langmuir isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 40 °C and pH 6

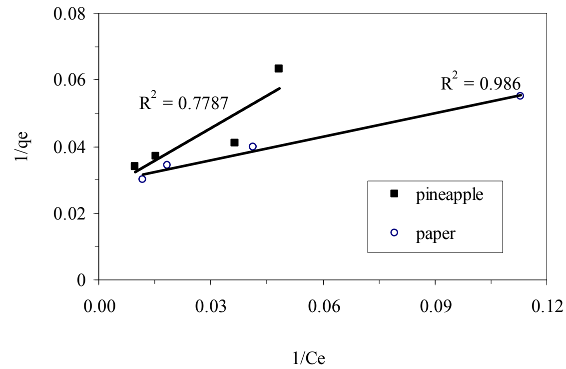

Fig. 7 Langmuir isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 50 °C and pH 6

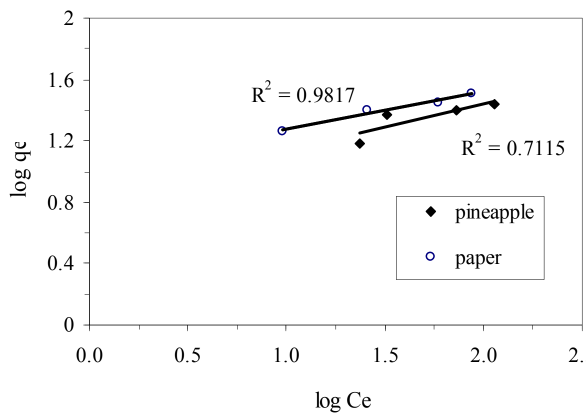

Fig. 8 Freundlich isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 30 °C and pH 6

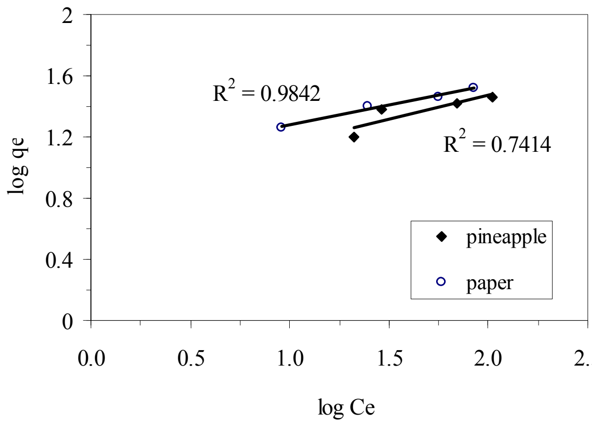

Fig. 9 Freundlich isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 40 °C and pH 6

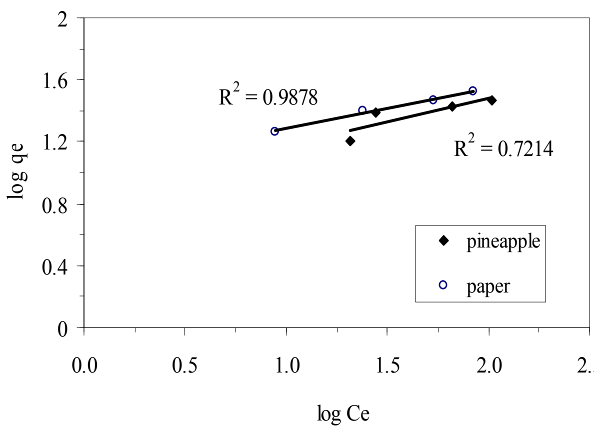

Fig. 10 Freundlich isotherm for lead adsorption onto pineapple and paper waste sludge 5 g·L^{-1} at 50 °C and pH 6

Table 1 The calculated Langmuir coefficients, correlation coefficient and separation factor at different temperatures, pineapple and paper waste sludge 5 g·L^{-1} and pH 6

Types of adsorbent	Temp (°C)	Langmuir			
		a_L	K_L	R^2	*SF*
pineapple	30	35.758	0.0375	0.7833	0.2105
	40	37.067	0.0407	0.8008	0.1973
	50	38.144	0.0409	0.7787	0.1966
paper	30	33.404	0.1227	0.9819	0.0753
	40	34.088	0.1239	0.9839	0.0747
	50	34.515	0.1246	0.9860	0.0743

Table 2 The calculated Freundlich coefficients, and correlation coefficient at different temperatures, pineapple and paper waste sludges 5 g·L^{-1} and pH 6

Types of adsorbent	Temp (°C)	Freundlich			
		n_F^{-1}	K_F	R^2	*SF*
pineapple	30	0.304	6.186	0.7115	0.001465
	40	0.309	7.069	0.7414	0.001413
	50	0.310	7.256	0.7214	0.001376
paper	30	0.251	10.481	0.9817	0.000953
	40	0.257	10.524	0.9842	0.000949
	50	0.260	10.543	0.9878	0.000948

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 two adsorbents 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.

Thermodynamic studies

Thermodynamic parameters such as Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) are calculated using the equations as follows:

$$\Delta G^{\circ} = -RT \ln K_L \tag{8}$$

$$\frac{\Delta G^{\circ}}{T} = \frac{\Delta H^{\circ}}{T} - \Delta S^{\circ} \tag{9}$$

where R is the universal gas constant (8.314 kJ·kmol^{-1}·K^{-1}), T is temperature in kelvin (K) and K_L is the Langmuir adsorption constant that can obtained from the equilibrium studies. The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be obtained from the slope and intercept of Van't Hoff from (9) as shown in Fig.7. The calculated thermodynamic constants at lead concentration 100 ppm, pH 6 and adsorbent 5 g·L^{-1} are listed in Table 3.

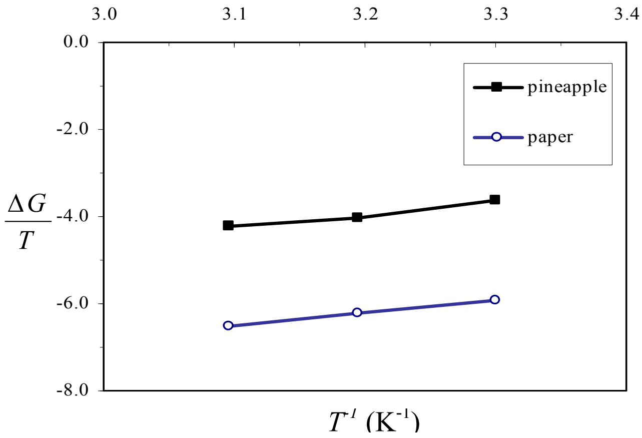

Fig. 11 Van't Hoff plot for different temperatures; lead concentration 100 ppm, pH 6, and pineapple and paper waste sludges 5 g·L^{-1}

Table 3: Thermodynamic parameters at different temperatures, lead concentration 100 ppm, pH 6, and pineapple and paper waste sludges 5 g·L^{-1}

Types of adsorbent	Temp (°C)	K_L (x10)	ΔG^o kJ·mol^{-1}	ΔH^o kJmol^{-1}	ΔS^o J·mol^{-1}·K^{-1}
pineapple	30	0.375	-3.648	5.1940	29.283
	40	0.407	-4.037		
	50	0.409	-4.230		
paper	30	1.227	-5.928	2.9107	29.190
	40	1.239	-6.237		
	50	1.246	-6.512		

The Gibbs free energy (ΔG°) is negative. It means that the adsorption process is spontaneous with high preference of lead for all adsorbents. The ranges of ΔG° values in this study are range from -3.648 to -4.230 kJ·mol^{-1} for pineapple waste sludge, and -5.928 to -6.512 kJ·mol^{-1} for paper waste sludge, which are in the range of physical adsorption. The calculated enthalpy (ΔH°) values of pineapple, and paper waste sludges were 5.1940 kJ·mol^{-1}, and 2.9107 kJ·mol^{-1}, respectively. The positive values of enthalpy show the endothermic reaction for the adsorption process, for which similar results have been obtained in the studies of Langmuir isotherm equation and separation factor. The reason may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [27]. The enthalpy (ΔH°) of pineapple waste sludge is lower than those of paper waste sludge.

The values of entropy changes (ΔS°) can be found 29.283 J·mol^{-1}·K^{-1}. for pineapple waste sludge, and 29.190 J·mol^{-1}·K^{-1} for paper waste sludge. The positive values of the entropy changes (ΔS°) show the higher randomness tendency at the absorbents and adsorbates interface during the lead adsorption onto waste sludge. Based on thermodynamics, negative ΔG° value and positive ΔH° and ΔS° values give a spontaneous process at high temperatures. The result is similar to other adsorbents [28, 29].

Kinetic Studies

Chemical kinetics is the area of chemistry concerned with speed, or rates, at which a chemical reaction occurs. The kinetic is the movement or change in concentration of reactant or product with time; therefore, kinetic refers to the rate of the reaction, or the reaction rate [30].

The rate constant of adsorption process carried out for different initial adsorbate concentrations and for different operation temperatures are determined in three types of adsorptions; zero order adsorption, first order adsorption, and second order adsorption [31].

Zero-order adsorption

Adsorptions whose order is zero are rare. The rate law of zero order is

$$Rate = \frac{dq}{dt} \tag{10}$$

$$\frac{dq}{dt} = k_{ad}[q_t - q_e]^0 = k_{ad} \tag{11}$$

where q_t, and q_e are amounts of lead adsorbed at time t and at equilibrium, respectively, and k_{ad} denote the adsorption rate constant. Thus, the rate of zero order adsorption is a constant, independent of amounts of lead adsorbed. Using the calculus with integration by applying the initial conditions $q = 0$ at $t = 0$ and $q = q_t$ at $t = t$, we can show that

$$(q_t - q_e) = q_e - k_{ad}t \tag{12}$$

The adsorption rate constant k_{ad} of zero-order adsorption can be calculated from the slope of (12).

First-order adsorption

A first-order adsorption is a adsorption whose rate depends on the amounts of lead adsorption raised to the first power. The rate is

$$\frac{dq}{dt} = k_{ad}[q_t - q_e] \tag{13}$$

After definite integration by applying the initial conditions q = 0 at t = 0 and q = q_t at t = t, the equation (13) becomes

$$\ln(q_t - q_e) = \ln q_e - k_{ad}t \tag{14}$$

The adsorption rate constant k_{ad} of first order adsorption can be calculated from the slope of (14).

Second- order adsorption

A second order adsorption is a adsorption whose rate depends on the concentration of one reactant raised to the second power. Te rate is

$$\frac{dq}{dt} = k_{ad}\left[q_t - q_e\right]^2 \qquad (15)$$

Using calculus, we can obtain the following expressions for the second order adsorptions:

$$\frac{1}{(q_t - q_e)} = \frac{1}{q_e} + k_{ad}t \qquad (16)$$

The adsorption rate constant k_{ad} of first order adsorption can be calculated from the slope of (16).

The linear relationship from three kinetic equations with different initial lead concentrations at 30 °C, pineapple and paper waste sludges are shown in Figs.12-17, respectively. The values of the adsorption rate constant, k_{ad}, of kinetic equations at different initial lead concentrations, pH 6, pineapple and paper waste sludges 5 g·L^{-1} are listed in Tables 4-6.

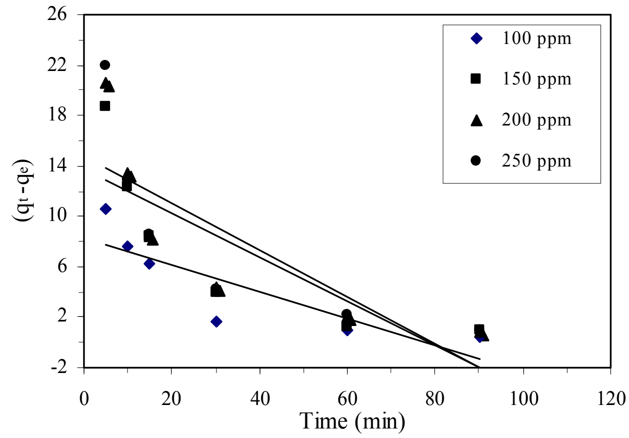

Fig. 12 Zero-order adsorption plots for various lead concentrations onto pineapple waste sludge, 30 °C, and pH 6

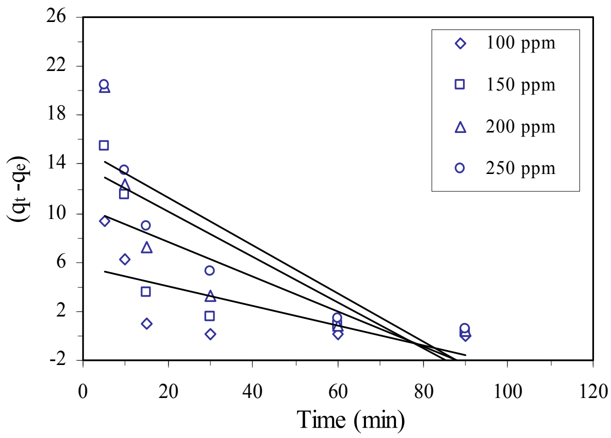

Fig. 13 Zero-order adsorption plots for various lead concentrations onto paper waste sludge, 30 °C, and pH 6

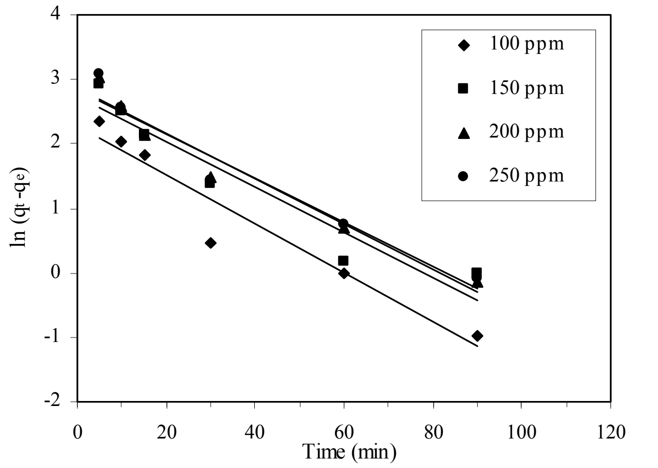

Fig. 14 First-order adsorption plots for various lead concentrations onto pineapple waste sludge, 30 °C, and pH 6

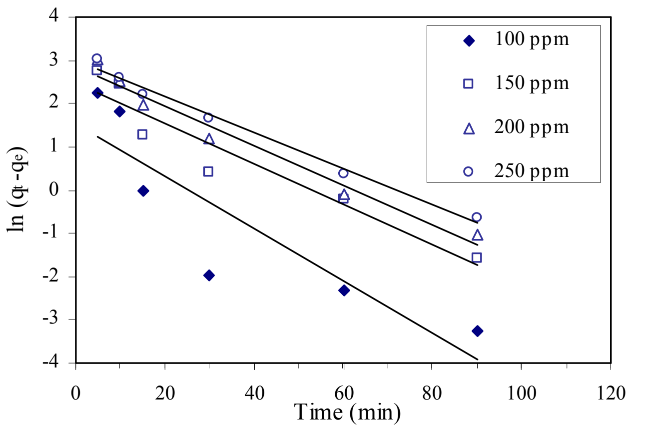

Fig. 15 First-order adsorption plots for various lead concentrations onto paper waste sludge, 30 °C, and pH 6

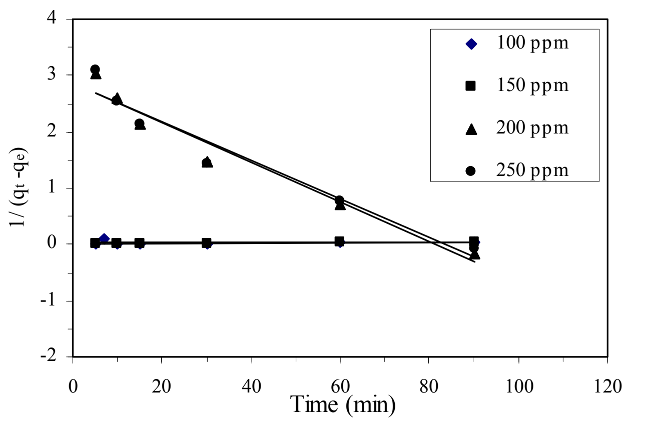

Fig. 16 Second-order adsorption plots for various lead concentrations onto pineapple waste sludge, 30 °C, and pH 6

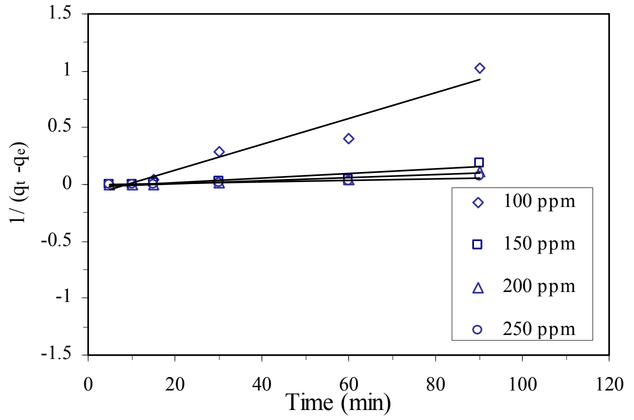

Fig. 17 Second-order adsorption plots for various lead concentrations onto paper waste sludge, 30 °C, and pH 6

Table 4 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in zero-order adsorption at different lead concentrations, pH 6, pineapple and paper waste sludges 5 g·L^{-1}, and 30 °C

Types of adsorbent	Concentration (ppm)	Zero-order adsorption	
		k_{ad}	R^2
pineapple	100	0.1061	0.7244
	150	0.1741	0.6914
	200	0.1868	0.6792
	250	0.1900	0.6435
paper	100	0.0809	0.4555
	150	0.1426	0.5536
	200	0.1856	0.6423
	250	0.1948	0.7262

Table 5 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in first-order adsorption at different lead concentrations, pH 6, pineapple and paper waste sludges 5 g·L^{-1}, and 30 °C

Types of adsorbent	Concentration (ppm)	First-order r adsorption	
		k_{ad}	R^2
pineapple	100	0.0382	0.9335
	150	0.0352	0.9163
	200	0.0351	0.9581
	250	0.0343	0.9451
paper	100	0.0605	0.7856
	150	0.0469	0.9117
	200	0.0463	0.9704
	250	0.0416	0.9872

Table 6 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in second-order adsorption at different lead concentrations, pH 6, pineapple and paper waste sludges 5 g·L^{-1}, and 30 °C

Types of adsorbent	Concentration (ppm)	Second-order adsorption	
		k_{ad}	R^2
pineapple	100	0.0011	0.9251
	150	0.0005	0.9654
	200	0.0005	0.9410
	250	0.0005	0.9474
paper	100	0.0114	0.9390
	150	0.0020	0.8522
	200	0.0013	0.9208
	250	0.0008	0.9064

Three adsorption equations have been tested, namely, zero-order, first-order, and second-order. The adsorption analyses based on the constant obtained from the linearized plots and R^2 show that the lead adsorptions onto pineapple waste sludge and paper waste sludge at different initial lead concentrations are first- and second-order adsorption. They are similar to other chemical reactions that the first- and second-order adsorptions are the most common adsorption types. The high R^2 values ($R^2 > 0.9$) indicate that the data could be well described by adsorption equation and show the first- and second-order nature of the process. A higher initial lead concentration had a smaller k_{ad} value in pineapple and paper waste sludges.

The linear relationship from three kinetic equations with lead concentration 100 ppm at different temperatures, pineapple and paper waste sludges are shown in Figs.18-23, respectively. The values of the adsorption rate constant, k_{ad}, of kinetic equations for lead concentration 100 ppm at different temperatures at pH 6, pineapple and paper waste sludges 5 g·L^{-1} are listed in Tables 7-9.

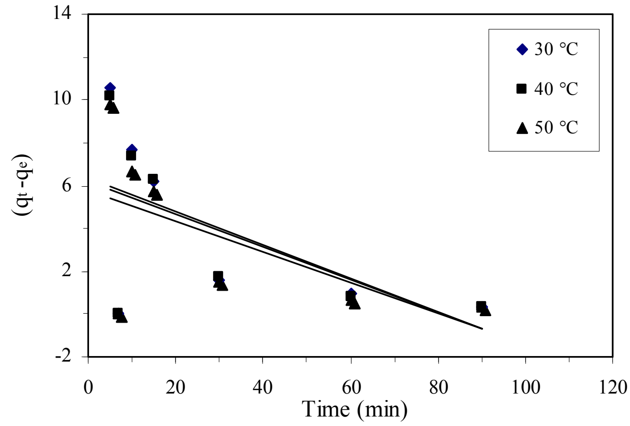

Fig. 18 Zero-order adsorption plots for various temperatures onto pineapple waste sludge, lead concentration 100 ppm, and pH 6

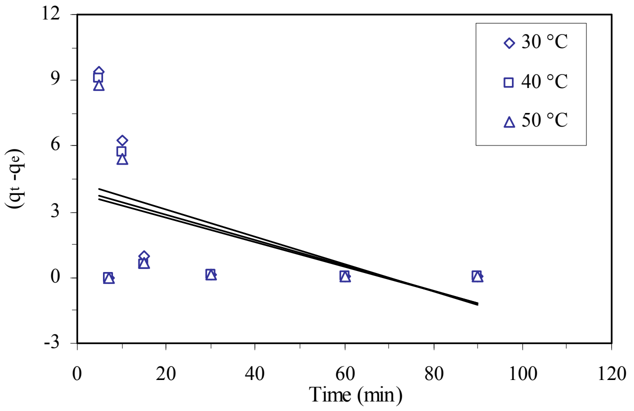

Fig. 19 Zero-order adsorption plots for various temperatures onto paper waste sludge, lead concentration 100 ppm, and pH 6

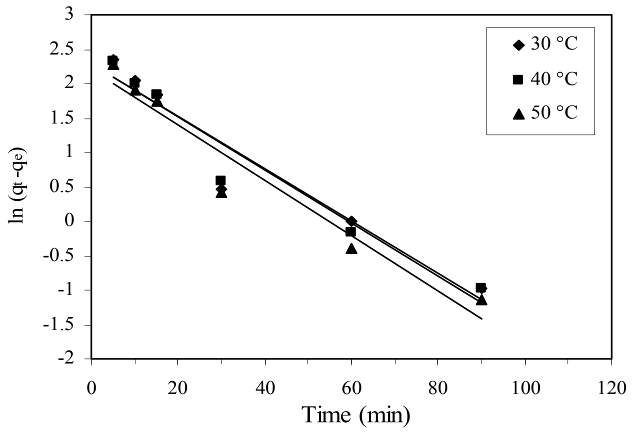

Fig. 20 First-order adsorption plots for various temperatures onto pineapple waste sludge, lead concentration 100 ppm, and pH 6

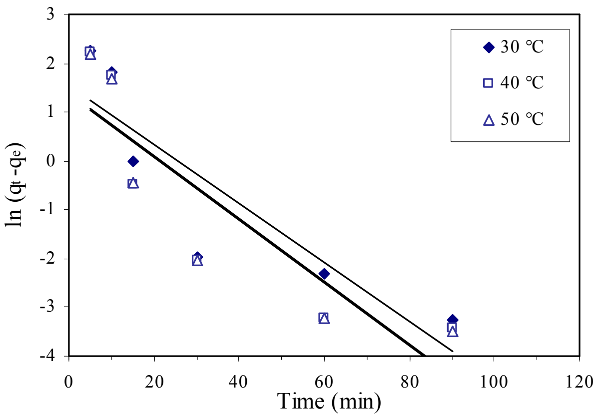

Fig. 21 First-order adsorption plots for various temperatures onto paper waste sludge, lead concentration 100 ppm, and pH 6

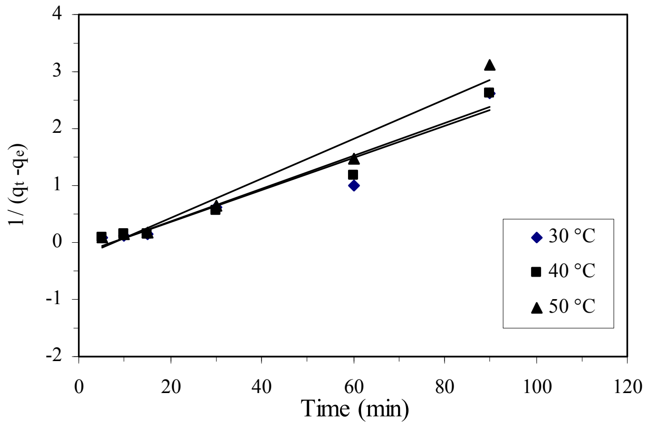

Fig. 22 Second-order adsorption plots for various temperatures onto pineapple waste sludge, lead concentration 100 ppm, and pH 6

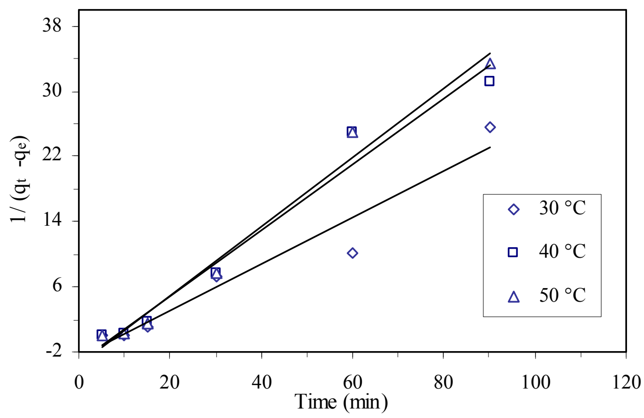

Fig. 23 Second-order adsorption plots for various temperatures onto paper waste sludge, lead concentration 100 ppm, and pH 6

Table 7 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in zero-order adsorption at different different temperatures, pH 6, pineapple and paper waste sludges 5 $g{\cdot}L^{-1}$, and lead concentrations 100 ppm

Types of adsorbent	Temperature (°C)	Zero-order adsorption	
		k_{ad}	R^2
pineapple	30	0.1061	0.7244
	40	0.1041	0.7438
	50	0.0981	0.7216
paper	30	0.0809	0.4555
	40	0.0762	0.4315
	50	0.0735	0.4331

Table 8 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in first-order adsorption at different temperatures, pH 6, pineapple and paper waste sludges 5 g·L^{-1}, and lead concentrations 100 ppm

Types of adsorbent	Temperature (°C)	First-order adsorption	
		k_{ad}	R^2
pineapple	30	0.0382	0.9335
	40	0.0387	0.9489
	50	0.0402	0.9426
paper	30	0.0605	0.7856
	40	0.0643	0.7720
	50	0.0646	0.7825

Table 9 The adsorption rate constant (k_{ad}) and correlation coefficient (R^2) of adsorption kinetics in second-order adsorption at different temperatures, pH 6, pineapple and paper waste sludges 5 g/L, and lead concentrations 100 ppm

Types of adsorbent	Temperature (°C)	Second-order adsorption	
		k_{ad}	R^2
pineapple	30	0.0011	0.9251
	40	0.0290	0.9274
	50	0.0348	0.9260
paper	30	0.0114	0.9390
	40	0.4045	0.9464
	50	0.4251	0.9448

The adsorption analyses based on the constant obtained from the linearized plots and R^2 ($R^2 > 0.9$) show that the lead adsorptions onto pineapple waste sludge at different initial lead concentrations and operation temperatures are first-order adsorption and onto paper waste sludge are first- and second-order adsorption. The increasing operation temperature improved the k_{ad} value.

The rate adsorptions increase with increasing temperature. The dependence of adsorption rate constant of a adsorption on temperature can be expressed by the Arrhenius equation as follows:

$$k_{ad} = Ae^{-E_a/RT} \tag{17}$$

Where E_a is the activation energy of the adsorption (kJ·mol^{-1}), R the gas constant (8.314 J·mol^{-1}·K^{-1}), T the absolute temperature (K) and e the base of the natural logarithm scale. The quantity A represents the collision frequency and is called the frequency factor. It can be treated as a constant for a given reacting system over fairly wide temperature range. The activation energy (E_a) is the minimum amount of energy required to initiate a chemical adsorption and can be determined by taking the natural logarithm of both side of (17):

$$\ln k_{ad} = \ln A - \frac{E_a}{RT} \tag{18}$$

The activation energy, E_a can be calculated from the slope of (18). The linear relationship from (18) for lead concentration 100 ppm with different temperature is shown in Fig. 22. The adsorption rate constants decrease with increasing temperature. The activation energy, E_a values are listed in Table 10.

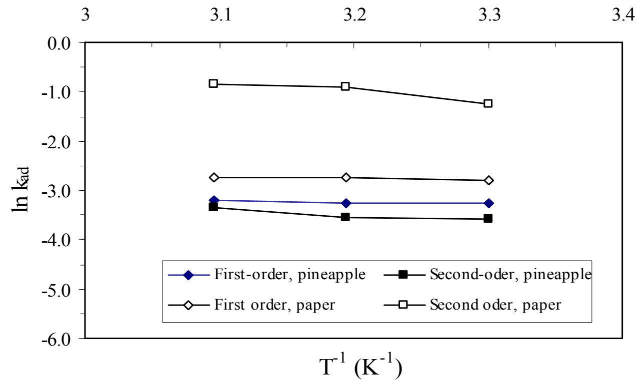

Fig. 22 Arrhenius plots the adsorption rate constant with different temperatures of first-and second-order adsorption, lead concentration 100 ppm, pH 6

Table 10 Activation energy (E_a) and correlation coefficient (R^2) from Arrhenius equation with first- and second-order adsorption, pH 6, pineapple and paper waste sludges 5 g·L^{-1}, and lead concentrations 100 ppm

Types of adsorbent	First-order		Second-order	
	E_a (J·mol^{-1})	R^2	E_a (J·mol^{-1})	R^2
pineapple	2.1542	0.9288	8.6891	0.8410
paper	2.6843	0.8225	16.3085	0.8550

The activation energy (E_a) of first-order adsorption onto pineapple waste sludge is lower than that of paper waste sludge. The higher *Ea* has affect to slowly equilibrium adsorption since rate constant is low. The *Ea* from first-order adsorptions onto both adsorbents are lower than those of second-order adsorption.

CONCLUSION

The results of this study show that the pineapple waste and paper waste sludges can be used as an effective adsorbent for lead removal in wastewater treatment. The Langmuir isotherm is better than fit equilibrium from Freundlich isotherm to describe the equilibrium adsorption the lead adsorption onto waste sludge based on linearized correlation coefficient. The endothermic adsorption on pineapple waste sludge is higher than that of paper waste sludge. The kinetic data obtained from different adsorption conditions are fit by the first- and second-order reaction. The applications of waste sludges to heavy metals removal is expected to be economical and effective. The new adsorbents from the natural sources and low cost for removing the heavy metals are our future works.

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