



Equilibrium Isotherm Modeling, Kinetics and Thermodynamics Study for Removal of Lead from Waste Water

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Abstract: The low cost adsorbent palm oil fuel ash (POFA) derived from an agricultural waste material was investigated as a replacement of current expensive methods for treating wastewater contaminated by Pb(II) cation. Adsorption studies were carried out to delineate the effect of contact time, temperature, pH and initial metal ion concentration. The experimental data followed pseudo second order kinetics which confirms chemisorptions. The values of Langmuir dimensionless constant, R_L and Freundlich constant, $1/n$ were less than 1 representing favorable process for adsorption. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° , related to Gibbs free energy, enthalpy and entropy were evaluated. It was concluded that, chemically treated palm oil fuel ash (POFA) can be used successfully for adsorption of Pb(II) from aqueous solution.

Keywords: Kinetics, Isotherm, Lead, Thermodynamics.

Introduction

The presence of heavy metal ions in natural or industrial waste water and their hazardous impact has generated considerable concern in recent years. As a consequence of several man-made factors such as unplanned urbanization, industrialization, deforestation *etc.* along with anthropogenic activities, there is a progressive increase in soil and water pollution by heavy metals such as arsenic, chromium, copper, lead, mercury, cadmium, nickel, zinc and iron *etc.*¹⁻³. There are several methods for waste water treatment such as ion exchange, adsorption, chemical precipitation, oxidation, reduction and reverse osmosis^{4,6}. However, many of these processes can be less effective or difficult for practical use due to their high price and sludge disposal problem. Therefore, to minimize this problem, lot of investigations has been carried out by the researchers to find out low cost, easily available materials from agricultural waste along with industrial by-products as adsorbents. Experimental adsorption

properties of numerous waste biomass have been reported, such as- wheat bran⁷, saw dust⁸⁻¹⁰, penicillium biomass¹¹, sunflower stalk¹², spent grain¹³, onion skin¹⁴, rice husk¹⁵⁻¹⁶, almond husk¹⁷, modified barks¹⁸, banana pith¹⁹, rice milling by- products (hulls and brans)²⁰ and soyabean hulls²¹ to remove heavy metals from waste water.

Malaysia has huge supply of waste biomass-generated from oil palm industries which consists of empty fruit bunch (EFB), palm shell (PS) and mesocarp fiber. This biomass is burnt in boiler to generate electricity which produces a lot of solid waste- palm oil fuel ash (POFA)²². Present work aims to remove Pb(II) cation from waste water by using chemically treated palm oil fuel ash and to investigate the physicochemical parameters involved during the sorption process. This research focuses on adsorption mechanisms, isotherm studies and evaluation of thermodynamic parameters for the sorption process of Pb(II) cation onto activated POFA from waste water.

Experimental

The palm oil fuel ash used here was taken from the middle of the flue tower where relatively fine ashes than the bottom layer is trapped before escaping from the burning chamber. The adsorbent thus obtained was sieved through sieve no 200 μm . It was washed with deionized water for several times to remove foreign particles and oven dried at 110 °C over night. 50 g of POFA were activated with 10 g of NaOH dissolved in 250 mL deionized water by refluxing the mixture at 160 °C for 8 h in a round bottom flask with a magnetic stirrer placed inside it. The slurry obtained was filtered and the filter cake was repeatedly washed with deionized water until neutral pH of the filtrate was observed. Then it was dried in an oven at 110 °C for 12 h before use and stored in desiccators for further application.

All reagents were of AR grade chemicals. Stock solution of lead nitrate, having concentration of about 1000 mg/L was prepared by using double distilled water. Various concentrations of test solution of lead ranging from 10mg/l to 70 mg/L were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 5.5 \pm 0.2 using a pH meter (Model CT No. CL 46, Toshniwal, India). Fresh dilution of the stock solution was done for each sorption study.

Each of the batch adsorption was carried out by contacting the NaOH modified POFA with the metal ion solution for a period of time in 100 mL plastic container by adding 0.2 g of adsorbent with 50 mL of different concentration of solution at 150 rpm. The residual concentration of Pb(II) was analyzed after definite interval of time until the system reached equilibrium by using atomic absorption spectrophotometer (Perkin - Elmer Model 3100). Experiments were conducted at 30 °C temperature to study the effect of initial pH, contact time and initial metal ion concentration. To study the effect of temperature, each experiment was carried out in a thermoregulated water bath (Haake Wia Model, Japan) with shaker cover in order to prevent heat loss to the surroundings. The equilibrium adsorption amount, q_e is calculated according to equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Here, q_e is the adsorption amount of metal ion (mg/g) at equilibrium contact time, W is the weight of adsorbent (g), V is the volume of solution (mL). Each experiment was triplicated under identical condition. C_0 is the initial concentration of the solution (mg/L) and C_e is the equilibrium concentration (mg/L). To minimize error, the mean value was used for calculation.

The removal efficiency of the metal ion was calculated by using equation (2):

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Results and Discussion

Surface characterization of the prepared adsorbent

The phenomenon of adsorption is largely dependent on surface area and pore structure. The specific surface area can be greatly increased by alkali treatment. Table 1 depicts the physical properties of activated POFA.

Table 1. Physical properties of activated palm ash

Adsorbent	BET surface area, m ² /g	Micropore area, m ² /g	Micropore volume, cm ³ /g	Mesopore volume, cm ³ /g	Average pore diameter (Å)
Activated POFA	467.1	561.9	0.199	0.349	46.9

Effect of initial metal ion concentration and contact time

Figure 1 shows the effect of initial metal ion concentration with equilibrium contact time. The maximum equilibrium uptake, q_e (mg/g) for Pb(II) was increased from 2.211 mg/g to 11.8088 mg/g for 10 mg/L to 70 mg/L respectively. This is because when the initial concentration of the solution was increased, the mass transfer driving force became larger, resulting greater adsorption capacity. All the concentration range studied here reached equilibrium within 90 minutes. However, the experimental data were measured for 180 minutes to ensure that full equilibrium was achieved. The removal % of Pb(II) was increased from 88.84% to 92.23% when the temperature was increase from 30 °C to 70 °C for 10 mg/L solution.

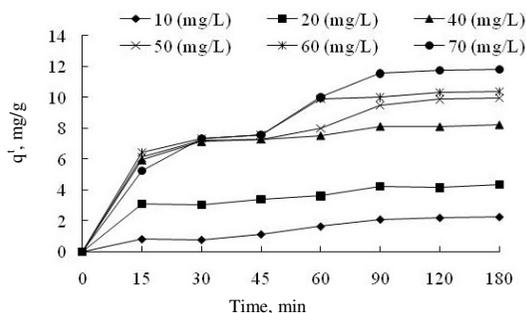


Figure 1. Effect of initial Lead ion concentration with equilibrium contact time at 30 °C

From the above figure, it is clear that the amount adsorbed, q_t (mg/g) increased with time and after certain time and it reached a constant value beyond which the uptake was more or less same. At the equilibrium point, the amount of lead adsorbing and desorbing from the adsorbent was in a state of dynamic equilibrium. The amount adsorbed at equilibrium time reflected the maximum adsorption capacity of the adsorbent under the operating conditions applied. The results revealed that lead adsorption was fast at the initial stage of contact period and thereafter it became slower near the equilibrium point. The initial faster rate may be due to the availability of the uncovered surface area of the adsorbent. After a certain period of time, the reactive sites were exhausted and then it became difficult for the adsorbate (lead) to occupy the adsorbent surface. At that moment repulsive force was present between the adsorbate adsorbed onto the adsorbent and the fraction of adsorbate remaining into the solution. Similar trend was observed for adsorption of lead and zinc onto natural goethite²³.

Effect of pH on equilibrium uptake

Figure 2 shows the percentage of Pb(II) cation adsorbed onto the modified surface of POFA as a function of pH. Maximum removal% was achieved between pH 4 to 6. For pH 2 to 3, the adsorption was low and it increased rapidly between pH 4 to 6. This phenomenon can be explained by the presence of H⁺ ions into the solution. When pH was less than 4, hydrogen protons were competing with metal ions for active binding sites on the surface of activated POFA. Fewer binding sites were available for Pb(II) cation to be adsorbed. As the pH increases from 2 to 4, there were fewer hydrogen protons in the solution. This means that there was less competition for binding sites. However, pH range of 4 to 6 was optimum for Pb(II) cation to be adsorbed by activated POFA. Thus adsorption of Pb(II) ions onto activated POFA was studied at pH 5.5±0.2 for subsequent experiments at equilibrium. At pH 8, the uptake of the cation started to increase. However, at higher pH, the cumulative effect of adsorption and precipitation of the ions may contribute to higher % of removal²⁴. Hence, the removal at high pH values was not studied.

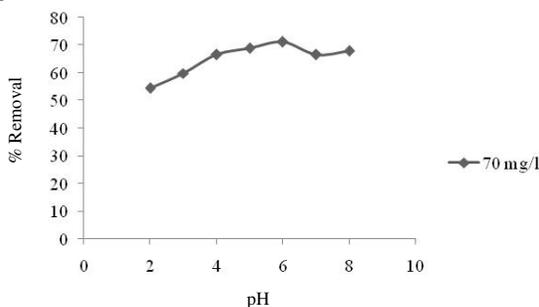


Figure 2. Effect of pH on removal % of lead: 0.2 g adsorbent agitated at 150 rpm with 50 mL solution of 70 mg/L lead at 30 °C

Study of adsorption kinetics

The study of adsorption kinetics is the main factor for designing an appropriate adsorption system and quantifying the changes in equilibrium uptake with time. Pseudo second order model which deals with chemisorptions can be expressed by following equations (3) and (4):

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 t \quad (3)$$

$$\frac{dq_t}{qt} = k_2 (q_e - q_t)^2 \quad (4)$$

Here, q_e (mg/g) and q_t (mg/g) are the amount adsorbed at equilibrium and at any time t , k_2 is the rate constants of pseudo second order reaction. The results obtained for adsorption of Pb(II) onto activated POFA was fitted with pseudo second order equation. Pseudo second order model provides correlation coefficient, R^2 nearer to unity for all the concentration range studied here except 10 mg/L. Moreover, the calculated values of q_e (mg/g) from pseudo second order agreed quite well with the experimental data. Hence it appears that, the system under consideration is more appropriately described by the pseudo second order model which was based on the assumption that the rate limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate²⁵. The initial sorption rate, h ($\text{mg g}^{-1} \text{min}^{-1}$) is $k_2 q_e^2$ for second order model. The kinetic parameters obtained are listed in Table 2.

Table 2. Pseudo-Second order kinetic parameters for adsorption of Pb onto POFA

Initial Concentration, mg/L	q _{e,cal} mg/g	q _{e,exp} mg/g	Rate constant, k ₂ , g- mg ⁻¹ min ⁻¹	h, mg-g ⁻¹ min ⁻¹	Correlation Coefficient R ²
10	3.1847	2.2211	0.0047	0.0477	0.896
20	4.6511	4.3435	0.0163	0.3526	0.995
40	8.5470	8.2041	0.0174	1.2710	0.999
50	10.9890	9.9693	0.0054	0.6521	0.994
60	11.3636	10.3625	0.0063	0.8135	0.993
70	13.8889	11.8088	0.0027	0.5208	0.987

Study of adsorption isotherm models

The study of the adsorption isotherm plays an important role in the determination of the maximum capacity of adsorption. Langmuir Isotherm model is given by following equation (5):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{5}$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \tag{6}$$

Here, q_e is the amount of equilibrium uptake (mg/g), C_e is the equilibrium cation concentration in solution (mg/L), q_{max} is the maximum monolayer adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (L/mg). The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given below:

$$R_L = \frac{1}{1 + K_L C_o} \tag{7}$$

C_o is the highest initial cation concentration (mg/L). The parameter R_L indicates the shape of isotherm and can be expressed as-

- Unfavorable (R_L > 1)
- Linear (R_L = 1)
- Favorable (0 < R_L < 1)
- Irreversible (R_L = 1)

The linear plots of Langmuir Isotherm at 30 °C temperature are shown by Figure 3. The model parameters at 30°C, 50°C and 70°C are listed in Table 3.

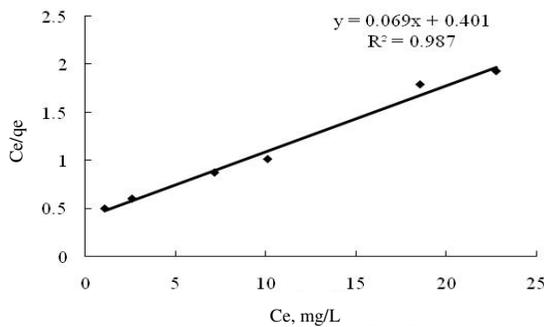


Figure 3. Adsorption isotherm obtained for Pb(II) sorption using Langmuir equation (linearized form) at 30 °C

Table 3. Langmuir constants at different temperatures for adsorption of Pb onto POFA

Temperature, °C	R_L	Maximum Adsorption Capacity, q_m , mg/g	K_L , L/mg	R^2
30 °C	0.76646	14.4927	0.1721	0.987
50 °C	0.073975	15.6250	0.1788	0.987
70 °C	0.052794	16.3934	0.2563	0.971

The reveals that separation factor; R_L is between 0.076-0.052 for all the temperature range studied here. This represents favorable adsorption. Maximum monolayer adsorption capacity, q_m (mg/g) increases with the increase of temperature from 30 °C to 70 °C which indicates endothermic nature of sorption²⁶. The Freundlich equation can be written by following equation (8):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

Equation (8) can be linearized to yield equation (9):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

Here, K_F (mg/g)(L/mg)^{1/n} and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. Freundlich isotherm model parameters for both the metals at 30 °C, 50 °C and 70 °C are summarized in Table 4.

Table 4. Freundlich Constants at different temperatures for adsorption of Pb onto POFA

Temperature, °C	Affinity Factor, K_F , mg/g(L/mg) ^{1/n}	Heterogeneity Factor, 1/n	R^2
30	2.4061	0.544	0.951
50	2.6326	0.547	0.962
70	3.4625	0.533	0.907

From the above table, it is clear that Freundlich exponent; 1/n is less than one which represents favorable adsorption process. The good agreement of the experimental data with the Freundlich model indicates surface heterogeneity of the adsorbent. The values of adsorption capacity, K_F increases with the increase of temperature. This represents that at higher temperature greater removal efficiency can be obtained. However, higher correlation coefficient, R^2 value is obtained from Langmuir model than Freundlich model for all the temperature range studied here.

Adsorption thermodynamics

The thermodynamic parameters including change in Gibbs free energy, ΔG° , enthalpy, ΔH° and entropy, ΔS° were determined by using following equations of (10) and (11):

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$\Delta G^\circ = RT \ln K_L \quad (11)$$

Here, K_L (L/mg) is the constant obtained from Langmuir isotherm. R (8.314 J/mol. K) is the universal gas constant and T is the temperature in Kelvin. ΔH° and ΔS° were calculated from the plot of $\ln K_L$ against $1/T$. The calculated values are given in Table 5.

Table 5. Thermodynamic parameters at different temperature

Temperature, °K	ΔG° , kJ mol ⁻¹	ΔH° , kJ mol ⁻¹	ΔS° , JK ⁻¹ , mol ⁻¹
303	-4.4344		
323	-4.6229	8.4636	0.0128
343	-3.9956		

The value of enthalpy change, ΔH° obtained here is 8.4636 kJ/mol. The positive value of enthalpy change confirms the endothermic nature of the adsorption process. The positive value of entropy, ΔS° corresponds to an increase in the degree of freedom of the adsorbed species. The positive value of ΔS° also reflects that some changes occur in the internal structure of palm oil fuel ash during the adsorption process. Similar types of observation were reported by other researchers for removal of lead and chromium from waste water²⁷. The magnitude of Gibbs free energy change, ΔG° obtained is negative suggesting that the adsorption is rapid and spontaneous. The negative value of ΔG° confirms feasibility of the process.

Conclusion

Palm oil fuel ash activated by sodium hydroxide has been shown to be a potentially useful material to remove Pb(II) from aqueous solutions. The rapid uptake and high sorption capacity along with its cheap cost make it a very attractive alternative sorbent material to treat waste water.

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