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# Equilibrium, Kinetic and Thermodynamic Studies of Lead Adsorption from Aqueous solution onto Activated Carbon Prepared from Silybum Marianum

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**Abstract :** In this study, Silybum Marianum leaves an agricultural waste was used to prepared low-cost activated carbon (AC) and test has efficiency to adsorb lead ions from aqueous solution by batch experiments under different condition of adsorbent weight, contact time, pH and initial lead concentration. Kinetic data obeyed to Ho-McKay pseudo second order equation. Freundlich and Langmuir isotherms were used to test the equilibrium data and the results shows better fit with a Langmuir equation with maximum adsorption capacity 76.34 mg/g. Thermodynamic parameter shows the adsorption of lead onto preparedAC was spontaneous and exothermic.

Keywords: Lead, Silybum Marianum, Adsorption, kinetic, Thermodynamic.

# **1. Introduction**

During the past century, a great deal of research has concern about the leadadverse effects specially on the human wherein, high levels of exposure attacks the central nervous system, brain and may cause death<sup>1</sup>. At the lowest level of exposure the haemoglobin synthesis, decreased, renal disease and other adverse effects<sup>2</sup>. The lead exposure comes from the use of lead in paint, pigment, battery manufacturing, fuel, solder, alloy and many other product<sup>3</sup>. Owing to the legislation restricting use of lead in fuel and as solder in the food industry as well as the low permissible value of lead in drinking water 0.01mg/L according to WHO (World Health Organization) the contaminated water become the main lead exposure<sup>4</sup>. Therefore, the removal of lead from waste water and drinking water is major interest in environmental research and variable methods were employed for that purpose, such as electro dialysis, chemical reduction, ion exchange, ultra filtration, adsorption and so in<sup>5</sup>. However, adsorption is a highly efficient method with the advantage of simplicity operation condition, sensitive to very low concentration, possibility of metal recovery, regeneration of adsorbent, and inexpensive<sup>6</sup>. The activated carbon used as adsorbent for a wide range of pollutants and due to the commercialactivated carbon is expensive the agricultural waste such as date stone, hazelnut shell, peach stone, rice husk, maize tassel, nut shells, corncob, coconut shell and almond shell, sugar cane were used to prepare the low cost activated carbon<sup>5-7</sup>.

This paper describes the preparation of activated carbon from SilybumMarianum leaves one of the wild plants grows normally in winter season in Iraq and test hasan efficiency for removal of lead from aqueous solution. The equilibrium, kinetic and thermodynamic parameters show the prepared activated carbon is an excellent adsorbent for removal of lead.

## 2. Materials and methods

#### 2.1. Preparation of activated carbon

The Silybum Marianum leaves were collected from Bismayah, Baghdad, Iraq. The leaves, washed with tap water to remove the dirt then with distilled water for three times and dried at room temperature for 3days. The dried leaves cut into small pieces and crushed by food processor, then impregnated with concentration solution of zinc chloride (1:1, by weight) the mixturestirring for 20 minthen dried at 377K for 24 hours. The dried sample placed in a closed container in muffle furnace and heated (5K/min) to 773K and held at the final temperature for 1hour. After cooling to room temperature the product washed with 0.5N HCl, then hot water and finally cold water to remove residual organic and mineral matters, then dried at 383K<sup>6</sup>.

## 2.2. Adsorption experiments

The (1000 mg/L  $Pb^{+2}$ ) Stock solution was prepared by dissolve 1.599g of lead nitrate (analytical reagent grade) in one liter of deionised distilled water. The 50ml of 50,100,150 and 200mg/Lof lead solution was prepared by dissolving appropriate amount of stock solution indistilled water and added separately to 250ml round bottom flasks. The pH was adjusted by using 0.1M of NaOH and HCl to the optimum pH and 0.4g of AC were added for each flask at 298K. The flask were shaken (thermostatically controlled shaker) for 90 min and then centrifugation (Lab. Centrifuge 80-2, China) for 5 min. The final concentration at equilibrium measured by Atomic Absorption Spectrometer(Perkin Elmer, model 500,US) and the amount of lead adsorbed on one gram of AC  $q_e$  and percentage removal calculated using the following equations<sup>3</sup>:

$q_e = \frac{C_o - C_e}{m} \ge V$	(1)
$\text{%Removal} = \frac{C_o - C_e}{C_o} 100$	(2)

Where,  $C_o(\text{mg/L})$  is concentration of lead before adsorption,  $C_e(\text{mg/L})$  is equilibrium concentration, m(g) adsorbent weight and V solution volume in liter.

## 3. Results and Discussion

#### 3.1.Effect of pH

The pH of the solution affected on electrical charge of adsorbent surface and the ionic forms of adsorbate molecule. Therefore, the adsorption of Pb (II) increases with decrease the acidity that is because in acid medium the hydrogen ion competed with Pb (II) molecule and as the number of hydrogen ion reduced more adsorption site will be free to adsorb Pb (II)<sup>8</sup>. Figure 1 shows the optimum pH is 7.



Figure.1.Effect of pH on percentage removal of 50mg/L initial concentration of Pb (II) at 298K

## 3.2.Effect of adsorbent weight

The influence of different weight of AC on lead percentage removal at a contact time 45 min was investigated by ranged the AC weight from 0.05g to 0.5g in 50mg/L lead solution. Figure.2 shows increased percentage removal with increasing of AC weight and that is because more surface area implies a greater number of adsorbent sites attained by increase the weight of  $AC^9$ .



Figure.2.Effect of adsorbent weight on percentage removal of 50mg/L initial concentration of Pb (II) at 298K

## 3.3.Effect of contact time and initial adsorbate concentration

The figure.3 Shows that the time required to reach the equilibrium is increasing with increase the initial concentration and that due to in low concentration the adsorbate adsorb on the outer surface site with a short period of time while for high concentration the diffuse of adsorbate molecules to the inner surface after saturation of outer surface required more time<sup>10</sup>. Figure.3 exhibit 45, 60, 70 and 90 min are the equilibrium time of 50, 100, 150 and 200 mg/L respectively.



Figure.3.Effect of contact time on percentage removal of different initial concentration of Pb (II) at 298K

## 3.4. Equilibrium isotherm

The equilibrium experimental data of adsorption of lead on AC derived from Silybum Marianum leaves were fitted to linear form of Freundlich and Langmuir equations. The Freundlich isotherm can be expressed in logarithmic form as follows<sup>11</sup>:

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

Where  $C_e$  (mg/L) lead concentration at equilibrium,  $q_e$ (mg/g) equilibrium uptake,  $K_F$  and  $\frac{1}{n}$  empirical constants exhibit the adsorption capacity and intensity, respectively. The value of these constants calculated from the slope and intercept of figure. 4. When the logs  $q_e$  Plotted against the logs  $C_e$ .

The Langmuir isotherm in linear form is given in the following equation<sup>12</sup>:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

Where  $C_e(\text{mg/L})$  lead concentration at equilibrium,  $q_e$  (mg/g) equilibrium uptake, the monolayer adsorption capacity  $q_m$  and Langmuir constant  $K_L$ Calculated from a linear plot of  $\frac{C_e}{q_e}$  against  $C_e$  as in figure5. The adsorption of lead on to AC follows Langmuir as well as Freundlich model and the Langmuir adsorption model appears better fit ( $R^2$ =0.9978) than the Freundlich model ( $R^2$ =0.9071).



Figure.4.Freundlich adsorption isotherm ofPb(II) onto AC at 298K



Figure.5. Langmuir adsorption isotherm of Pb(II) onto AC at 298K

Table. (1): Isotherms constants and correlation coefficient

Langmuir isotherm			Freundlich isotherm			
$K_L$ (L/mg)	$q_m (mg/g)$	R <sup>2</sup>	$K_F$	1/n	R <sup>2</sup>	
			$(mg/g(\frac{L}{mg})^{1/n})$			
0.0422	76.34	0.9978	10.6440	0.3620	0.9071	

## 3.6.Adsorption kinetic

The pseudo first order (Lagergren equation) and (Ho equation) pseudo second orderwere used to test the kinetic data in order to understand the dynamic of adsorption reaction. These equations can be represented respectively as follows<sup>13</sup>:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
 (6)

Where,  $q_e$  and  $q_t$  the quantity of lead adsorbed on one gram of AC at equilibrium and time t respectively. From plot of log  $(q_e-q_t)$  against t(figure.6) and  $\frac{t}{q_t}$  against t (figure.7) the rate constant and equilibrium uptake for this equation can be obtained.

The determination of suitable kinetic model for the adsorption reaction by comparing the correlation coefficient is restricted to linear kinetic model. Therefore, thesum of error squares used to indicate the most suitable kinetic mode [9]:

SSE (%) = 
$$\sqrt{\frac{\Sigma(q_{e,exp}-q_{e,cal})^2}{N}}$$
 (7)

Where SSE is sum of error squares,  $q_{e,exp}$  experimental equilibrium uptake,  $q_{e,cal}$  calculated equilibrium uptake and N number of data points. The result in table2 shows correlation coefficient close to 1 and sum of error squares close to zero for pseudo-second order that conform the adsorption of lead onto AC is follows pseudosecond order under the condition used in this study.



Figure.(6): Pseudo-first order of Pb(II) onto AC at 298K



Figure.(7): Pseudo-second order of Pb(II) onto AC at 298K

$q_{e,exp}$	Pseudo-first order			Pseudo-second order				
mg/g	$k_1(min^{-1})$	<i>q<sub>e,cal</sub></i>	$R^2$	%SSE	$k_2$	q <sub>e,cal</sub>	$R^2$	%SSE
		mg/g			$g.mg^{-1}.min^{-1}$	mg/g		
15.79	0.0843	6.516	0.969	8.484	0.0230	15	0.999	0.79

## **3.7.Thermodynamic studies**

Thermodynamic parameters are calculated by following equations<sup>4</sup>:

$$K_{c} = \frac{c_{ads}}{c_{e}} = \frac{c_{o} - c_{e}}{c_{e}} = \frac{c_{o}}{c_{e}} - 1 \quad (8)$$
$$\Delta G^{o} = -RT \ln K_{c} \quad (9)$$
$$\ln K_{c} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \quad (10)$$

Where,  $K_c$  equilibrium constant,  $C_o(\text{mg/L})$ ,  $C_{ads}(\text{mg/L})$ , and  $C_e(\text{mg/L})$  represent the originallead concentration, concentration of adsorbed lead and remaining concentration in solution at equilibrium, respectively. The  $\Delta G^o$ ,  $\Delta H^o$  and  $\Delta S^o$  are changes in free energy, enthalpy and entropy respectively. R gas constant (8.314J.mol<sup>-1</sup>.K<sup>-1</sup>) and T (K) solution absolute temperature. The  $\Delta G^o$  obtained have negative signs that indicate the adsorption process was spontaneous and from the slope and intercept of van'tHoff plot (Figure.8),  $\Delta H^o$  and  $\Delta S^o$  are calculated. The thermodynamic results summarized in table3.showsnegative value of enthalpy indicates an exothermic adsorption reaction and negative value of entropy indicate decrease in randomness



Figure.8Van't Hoff plot of Pb(II) onto AC.

Table.(3): Values of thermodynamic parameters for the adsorption of Pb(II) onto AC

T(K)	$\Delta G(kJ.mol^{-1})$	$\Delta \mathbf{H}(\mathbf{kJ}.mol^{-1})$	$\Delta S(J.mol^{-1}.K^{-1})$
298	-5.443		
308	-5.353		
318	-5.168	-1.15	-20.32
328	-4.816		

## **4.**Conclusion

The results exhibit that ACprepared from SilybumMarianum leaves is an excellent new low cost adsorbent for removal of Pb(II) from aqueous solution. The experimental equilibrium data obeyed for Langmuir as well as Freundlich isotherms with better fit to Langmuir isotherm. Thermodynamic studies show the adsorption process spontaneous and exothermic.

# References

- 1. Childhood lead poisoning, WHO, Geneva 2010, page: 25,55.
- 2. Guidelines for drinking water quality, WHO, Geneva, 2010, page: 383.
- 3. Awual, M.R. "Assessing of lead(III) capturing from contaminated waste water using ligand doped conjugate adsorbent" chemical engineering J, 289(2016) 65-73.

- 4. Hikmat, N.A.; Qassim, B.B. and Khethi, M.T. "Thermodynamic and kinetic studies of lead adsorption onto petiole and fiber of palm tree" American journal of chemistry,4(4),(2014), 116-124.
- 5. Baccar, R.; Bouzid, J.; Feki, M. and Montiel, A. "Preparation of activated carbon from Tunisian olivestone waste cakes and its application for adsorption of heavy metal ions" Hazardous materials J, 162(2016), 1522-1529.
- 6. Sahu, J.N; Jyotikusum, A.; Sahu, B.K and Meikap "Optimization of lead (II) sorption potential using developed activated carbon from Tamarind wood with chemical activation by zinc chloride" Desalination and water treatment J,57(2016), 2006-2017.
- 7. AL-Tufaily, M.A. and AL-Qadi, Z.S "Preparation and utilization of corncob activated carbon for dyes removal from aqueous solution batch and continuous study" Babylon university engineering science J, 24(3),(2016), 700-712.
- 8. Farha, A.M.; Jassim, R.A. and Kadhim, N.J. "The removal of zinc from aqueous solution using Malvaparviflora" Baghdad science journal, 13(3), (2016), 482-488.
- 9. Kareem, K.A. "Removal and recovery of methylene blue dye from aqueous solution using Avenafatua seed husk" Ibn Al-Haitham journal for pure and applied science, 29(3), (2016), 120-138.
- 10. Santhi, T.; Manonmani, S.; Vasantha, V.S. and Chang, Y.T. "A new alternative adsorbent for the removal of cationic dyes from aqueous solution" Arabian journal of chemistry, 9, (2016), 466-474.
- 11. Freundlich, H. "Over the adsorption in solution" Z.Phys.Chem. J, 57, 385-470,1906.
- 12. Langmuir, I."The adsorption of gases on plane surfaces of glass, mica and platinum"Am.Chem. J,40(9),1361-1403,1918.
- 13. HO, Y.S. and Mckay, G. "The sorption of lead (II) ions on peat" Wat. Res.J, 33(2),(1999), 578-584.

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