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Equilibrium and Kinetic Study for Adsorption of Lead using Packed Column by *Acidified Neem Saw Dust*

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Abstract: The industrial wastewater released into the environment causes water pollution. High content of toxic metals in the water is a main criteria for the water pollution. Lead is one of the toxic metal present in wastewater at a high rate. Hence, Removal of lead is considered to be a best reason to maintain hygienic environment. Removal of lead is found to be more efficient using packed adsorption processes by acidified neem saw dust. Adsorption kinetics, Thermodynamics parameters like Free energy (ΔG),Change in Enthalpy (ΔH), Change in Entropy (ΔS) were observed. Experimental data is carried away for Langmuir, Freundlich and Temkin isothermal models and the overall yield at a rate of 6.493 mg/gm shows the best fit in Langmuir model.

Keywords: Lead, Enthalpy, Entropy, Free energy, Acidified Neem Saw Dust, Isothermal models.

INTRODUCTION

Lead is a problematic metal [1] present is highly abundant in e-waste. Mostly non-carcinogenic toxic effects of several metals include arsenic, cadmium, chromium, nickel, zinc, lead [2], mercury and barium. lead accumulated in the environment and produce both high acute and chronic effects on biological system [3] (i. e. plants, animal and microorganism). Removal of lead is considered to be important due to its carcinogenic effects. The natural techniques and adsorbents used are environmental friendly. Among other processes for removal of heavy metals from industrial effluent,[4] adsorption has been shown as the most appealing in terms of economic and an environmental friendly procedure. adsorption is a mass transfer process[5,6] by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical or chemical interactions.

EXPERIMENTAL PROCEDURE

COLLECTION OF ADSORBENT:

Saw dust is collected from the mill in and around Visakhapatnam.

PREPARATION OF ACIDIFIED ADSORBENT:

Crude extract of saw dust of 175 gm are collected and dried for a while. The dried sample is then cleaned and kept in a plate. Add 500 ml of 1N H_2SO_4 into it and then acidification process is carried away for 24 hrs. Finally, They are dried in a hot air oven at 100℃ for 2 hrs and sieved it through 200 mesh size for equal consistency.

COLLECTION OF SAMPLE:

Industrial wastewater was collected from beach area around Visakhapatnam.[7]

PROCEDURE

A glass column made of Pyrex with dimensions 50 cm height and 5 cm inner diameter are taken and stopcock is adjust tightly at the top of the column [8]. Glass column are packed by glass wool and beads tightly in a uniform manner. 73 micron size of prepared acidified neem saw dust is then poured into it and set for uniformity. The column is gently settled and the bed arranged is pressed with a glass rod to maintain its consistency as shown in Fig. 1.The Weight of the saw dust packed in the column are recorded [9]

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Fig.1 Column packed with Acidified Neem Saw Dust

The lead sample solution of 50mg/L concentration is allowed to flow continuously through a saw dust packed column using a peristaltic pump at a rate of 2mL/min.[10] The adsorption process of saw dust is carried away and the finally treated lead sample is collected from the bottom with a help of outlet arranged as shown in above figure. The performance of lead concentration after treated through the fixed bed column of saw dust was studied. The treated sample solutions are collected at every 30 min interval using UV visible spectrophotometer. This process is continued till the concentration of outlet and inlet concentration equalized.[11]

RESULTS AND DISSCUSION

Adsorption of lead is carried out using packed column by acidified neem saw dust.

ADSORPTION ISOTHERMS:

1.1. LANGMUIR ISOTHERM

The Langmuir sorption isotherm has been successfully applied to many pollutant adsorption processes and has been the most widely used isotherm. Langmuir theory is based on the assumption that the adsorption takes place at specific homogeneous sites within the adsorbent.[12]

The Langmuir equation is given as:

$$(C_e/q_e) = 1/(q_{max}.b)+(C_e/q_{max}) \qquad (1)$$

Where,

Ce = concentration of the dye solution at equilibrium (ppm)

qe = amount of dye adsorbed at equilibrium, (mg/g)

qmax = maximum sorption capacity, (mg/g)

b = Langmuir constant (L/mg)

Fig. 2 shows the plot of the Langmuir equation (1), (C_e / q_e) vs (Ce), which indicates a straight line with a slope of $1/q_{max}$ and an intercept of $1/bq_{max}$. From the plot of Langmuir equation, the maximum adsorption capacity (q_{max}) is found to be 6.493 mg/g and Langmuir constant (b) is found to be 0.1480 L/mg.

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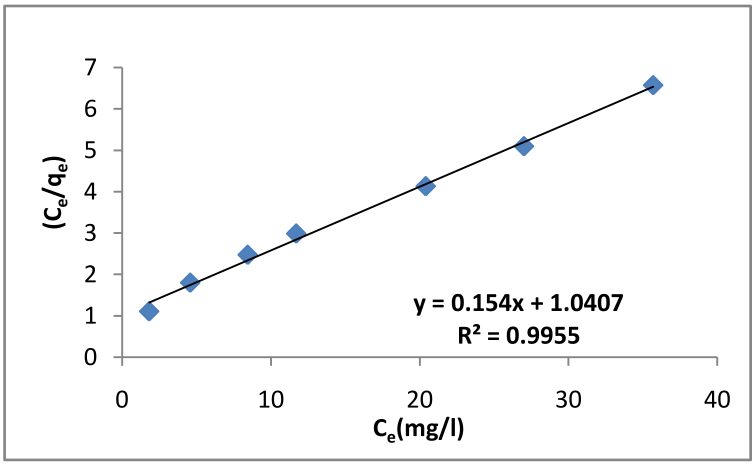

Fig.2 Langmuir Isotherm for adsorption of lead

1.2. FREUNDLICH ISOTHERM

Freundlich isotherm states that, when the concentration of solute in the solution at equilibrium (C_{eq}) is raised to the power m, the amount of solute adsorbed being q_{eq}, then $C_{eq}m$ /q_e is a constant at a given temperature, which is expressed by the following equation:

$$\log q_e = \log K_F + (1/n) * \log C_{eq} \qquad (2)$$

Fig. 3 shows the plot of log q_{eq} vs log C_{eq}. From the plot, the adsorption / distribution coefficient (K_F) is found to be 1.101 and the value of (n) is 2.252

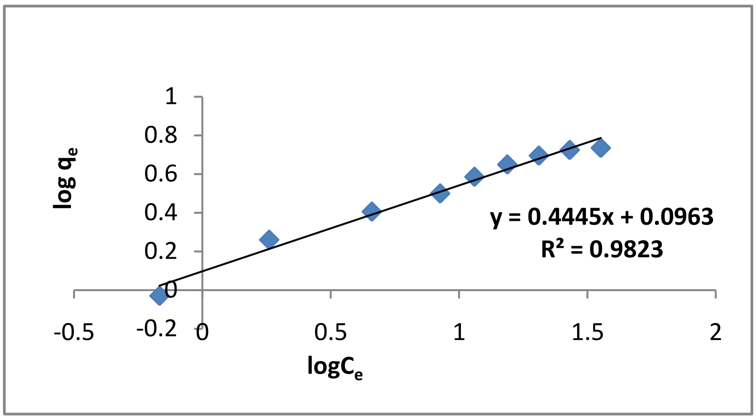

Fig.3 Freundlich isotherm for adsorption of lead

1.3. TEMKIN ISOTHERM: This model takes into account the presence of indirect adsorbate / adsorbent interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage. Temkin isotherm is given as:

$$q_e = B \ln C_e + B \ln k_T \qquad (3)$$

Here $B=RT/b_T$

Where, b_T and K_T are Temkin isotherm constants.

Fig. 4 shows a plot of q_{eq} vs ln C_{eq}, which is a straight line with slope of RT/b_T and intercept of $B\ln K_T$.

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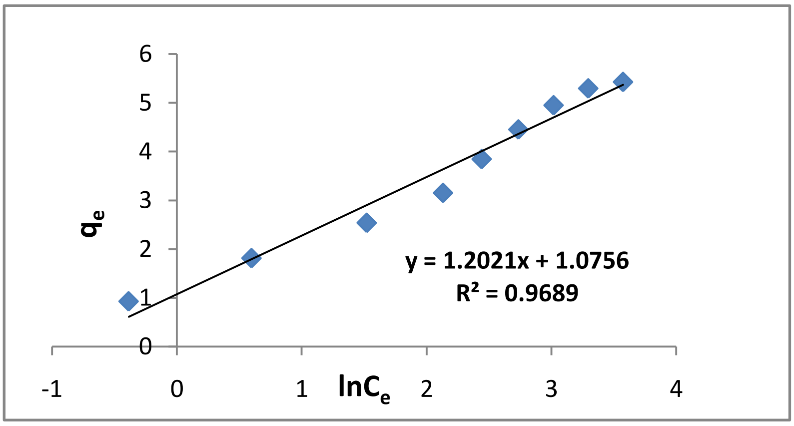

Fig.4 Temkin Isotherm for adsorption of lead

From the plot, Temkin constants are found as b_T =2095.79 J/mol and K_T = 2.445 L/mg with R^2value =0.9689

The isotherm constants obtained from the above three isotherms are compiled and listed in Table-1. The best fit equilibrium model is determined based on the linear regression coefficient (R^2). From the table, it is observed that the adsorption data are well represented by both Langmuir and Freundlich isotherms for Acidified saw dust dye adsorption with higher R^2 of 0.995, 0.9823followed by Temkin isotherm with R-squared value of 0.9689.

Table-1: Isotherm constants

Langmuir model	**Freundlich model**	**Temkin model**
q_{max} = 6.493 mg/g	1/n = 0.444	b_T = 2095.79 J/mol
b = 0.1480 L/mg	K_F = 1.101	K_T = 2.445 L/mg
R^2 = 0.995	R^2 = 0.9823	R^2 = 0.9689

2.0. KINETIC STUDIES:

The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first order and pseudo-second order. These models correlate solute uptake, which are important in predicting the reactor volume [13].

2.1. PSEUDO-FIRST ORDER MODEL

The possibility of adsorption data following Lagergren pseudo-first order kinetics is given by

$$dq/dt = k_1 (q_{eq}-q)$$

$$\ln(q_{eq}-q_t) = -k_1t+\ln q_e \qquad (4)$$

Where q is the amount of adsorbate at time t (mg/g), q_{eq} is the adsorption capacity at equilibrium (mg/g), K_1 is the rate constant of the pseudo-first-order model (min^{-1}). Values of rate constant (K_1) and q_{eq} for adsorption of dye are determined from the plot of ln (q_{eq}-q_t) vs. time (t), shown in Fig 5. The intercept of the plot is equal to ln q_e. The correlation coefficient for pseudo first order is 0.9883.

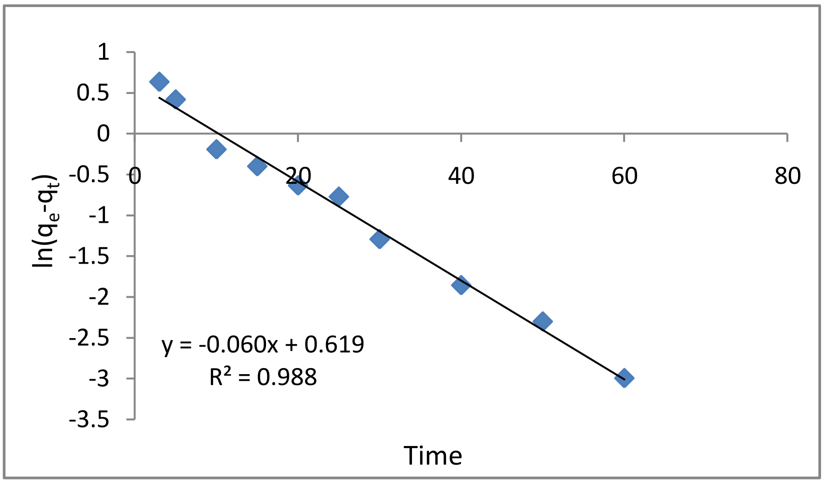

Fig.5 First Order kinetics for adsorption of lead

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2.2. PSEUDO-SECOND ORDER MODEL

A pseudo-second order model proposed by Ho and McKay was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorptions. The pseudo-second order model can be expressed as

$$dq/dt = K_2 (C_{eq}-q)^2 \qquad (5)$$

Separating the variables in Eq. (5) gives

$$(dq)/((C_{eq}-q)2) = K_2 dt \qquad (6)$$

Integrating Eq. (6) for the boundary conditions q=0 to q=q at t=0 to t=t, Eq. (6) simplifies to

$$(t/q_t) = (t/q_e) + 1/(k_2.q_e 2) \qquad (7)$$

Where t is the contact time (min), q_{eq} is the amount of dye adsorbed at equilibrium (mg/g) and q is the amount of dye adsorbed at any time, t (mg/g). The correlation coefficients were found to be 0.9991 for initial concentrations 10 ppm to 50 ppm. If second order kinetics is applicable, the plot Fig. 6 of t/q_t versus time (t) of equation (7) should given a linear relationship from which the constants q_{eq} and K_2 can be determined

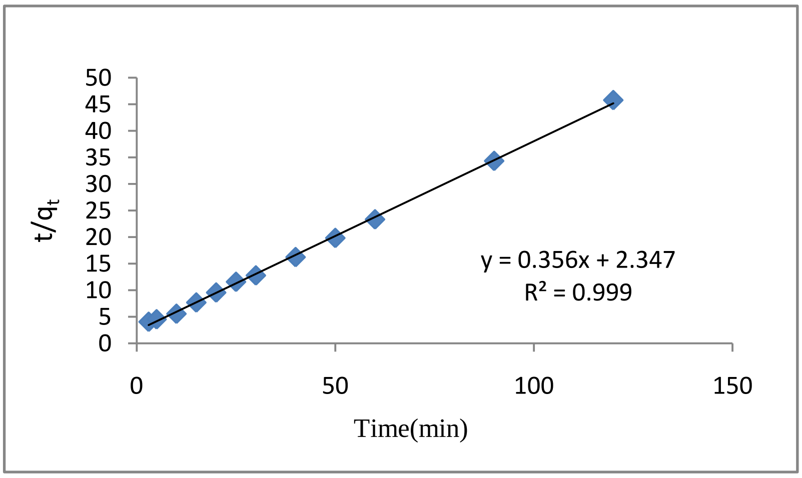

Fig:6 : Second Order kinetics for adsorption of lead

3.0 Effect of Thermodynamic parameters:

The change in variation of adsorbed amount during adsorption can be explained by three main thermodynamic parameters. These parameters are entropy change (S), enthalpy change (H) and Gibb's free energy (G). The negative value of ΔH indicates that the process is exothermic and the positive value of ΔH indicates that the process is endothermic. The thermodynamic parameters for the adsorption process were computed from the plot of ln (C_S/C_{eq}) vs. 1/T, shown in Fig. 7, here $(K_C = C_S/C_e)$.

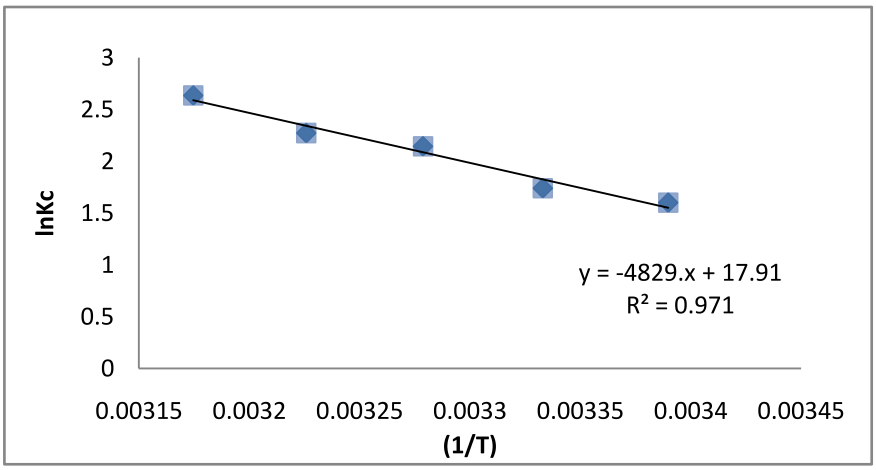

Fig.7 Effect of temperature with respect to concentration for adsorption of lead

The free energy change for lead ions on to acidified neem saw dust were determined using the equilibrium constant obtained from surface concentrations at each initial concentration.

From plot, slope (ΔH/R)=4829 J/mol and Thermodynamic parameters values are listed in the Table -2.

Table.2.Thermodynamic parameters values for adsorption of lead

S.NO.	Temperature(K)	lnK	ΔH (kJ/mol)	ΔG= (-RT lnKC) (kJ/mol)	ΔS =(ΔH-ΔG)/(T) (kJ/mol.k)
1	315	2.633	40.150	-6.897	0.1493
2	310	2.271		-5.854	0.148
3	305	2.142		-5.433	0.1494
4	300	1.738		-4.336	0.1482
5	295	1.599		-3.923	0.1494

CONCLUSION

According to present study, the heavy metals from industrial wastewater cause water pollution. Lead is considered to be one of the toxic metal leads to many disorders .Hence, adsorption of lead using packed column by acidified neem saw dust is considered to be the best and effective process. The removal of lead is performed and its isotherms are plotted to justify the highest percentage removal rate. All the Isotherms like Langmuir, Freundlich and temkin are preformed and plotted, Langmuir has shown the best fit at an yield of 6.493 mg/gm and various thermodynamic parameters are calculated, R^2 = 0.971.Finally, The kinetics performed declares that the adsorption process using acidified saw dust is considered to be an effective for pseudo second order kinetics method at a high removal rate. and for free energy indicates negative values in above table means the adsorption process is spontaneous and also calculated entropy change is positive values means the disorderness at solid-liquid interface is increased.

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