

Adsorption of Lead from Aqueous Solution by Hybrid Precursor from Rice Husk

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Abstract: A carbon adsorbent derived from rice husk by nitric acid treatment was used for the removal of Pb (II) from aqueous solution. Sorption of metal ion has been studied as a function of contact time, temperature, pH of the solution and metal ion concentration. These factors have remarkable positive effect on sorption process. The adsorption data of RHHP at different initial concentration was fitted to Freundlich & Langumir adsorption isotherms and monolayer sorption capacity determined was 72.04 (pH 6.0 temperature 20⁰c). Thermodynamic Parameter indicated that the sorption is exothermic, spontaneous with a greater affinity of metal species for the adsorbent.

Keywords: Rice husk hybrid precursor (RHHP), Pb(II), Sorption, Metal ion, adsorption isotherm, AAS

1. Introduction

The heavy metal plays a vital role in the normal functioning of living organism. Yet imbalance of any of the heavy metals will disturb above function. Most of the reported work on the use of agricultural by-products for removal of heavy metals has to do with the capability of such materials in adsorbing heavy metals¹. The principle behind exploring agricultural by-products in this work is the fact that most agricultural by-products are composed of cellulose in the plant cell walls. A number of methods are available for the removal of metal ions from aqueous solutions. Processes including chemical precipitation, Coagulation, Solvent extraction, electrolysis, membrane separation, ion exchange and adsorption are commonly used to solve pollution problems caused by heavy metals. For this purpose, activated carbon adsorption is well known method for removal of heavy metals^{2,3,4} but the high cost of activated carbon restricts its large-scale use for the abatement of heavy metal pollution in developing countries. Therefore the application of these processes is sometimes restricted, due to technical and economic restrictions⁵.

Activated carbon is manufactured from variety of sources primarily coal, wood, lignite and coconut shell etc. While agricultural by-products as precursors for the preparation of activated carbon have minimum cost, the benefits of the preparation of activated carbon from agricultural by-products wood also include removal of polluting waste product and economic gains for products manufactured from abundant sources. It has been reported that activated carbons have been prepared from the following precursors: coconut shells and wood^{6,7} almond shells, plum stones, cane baggage and banana pitch and rice husks⁸.

Activated carbons are unique and versatile adsorbent because of their large surface area, micropore structure, varied adsorption effect and high adsorption capacity. Commercially available activated carbons are expensive & their use requires elaborate regeneration and reactivation procedure. The gradual

loss of activated carbon during regeneration can materially affect the economic viability of the process⁹.

Lead is a bluish-grey metal with a high density. It readily dissolves in medium concentrated nitric acid and nitrogen oxide gas. When needed with air, is oxidized to red nitrogen oxide with concentrated nitric acid a protective film of lead nitrate is formed on the surface of the metal and prevent further dissolution.

Lead poisoning (also known as plumbism) is a medical condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death.

2. Experimental

- **Preparation of the sample:** The RHHP is prepared by Standard Novel method.
- **Preparation of Lead Stock solution:** For our analytical purpose we made a stock solution of lead of 1000 ppm from lead nitrate. For this purpose we dissolve 1.30 gm in 100 ml of water All reagent are AR or GR Grade.
- **Sorption Studies:** For the study of removal of Pb(II) metal from aqueous solutions 100 ml of metal solution is taken with 2.5 gm of hybrid precursor in a shaker (100 rpm.). After about 45 minutes samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual metals by AAS.

3. Results and Discussion

The results obtained from AAS Study is shown in table 1 and it is evident that the adsorption of Pb(II) is maximum at this concentration and at pH 6.0. The Contact time was 45 minutes.

3.1 Effect of contact time on Pb (II) uptake

Using Batch technique the dependence of adsorption of Pb(II) on contact time was determined at time intervals of 15 minutes, 30 minutes, 45, 60, 75, 90 and 105 minutes at 293K & 313K. The table 1 & 2 shows the effluence of contact time on the adsorption of metal by hybrid precursor made from Rice husk. Effect of contact time was studied by taking 1000 ppm metal solutions at pH 6.0 (adsorbent dose 2.5 gm.). Rate of uptake of Pb (II) was initially higher and increases with contact time it ranges from 26.54 to 70% at 293K and at 313K the Percent removal ranges from 29.04 to 72.04. The increase in removal efficiency with contact time is due to the increase in surface area and hence more active sites are available for the adsorption. The figure 1 and 2 shows the dependence of adsorption of metal ion on contact time and indicates that contact time plays a vital role in any adsorption process.

3.2 Effect of pH on Pb (II) uptake

Aliquots of 100 ml Pb (II) solution of known concentration were poured into beaker (250ml) containing accurately weighted amounts of adsorbents. The RHHP weight was 2.5gm. The beaker glasses was shaken at 200 rpm using an electric shaker for 12 hour's at 293K. The solution was centrifuged and adsorbent was then removed by filtration. After filtration the solution was analyzed for residual metal content by AAS. A series of solution of hybrid Rice Husk hybrid Precursor (RHHP) with metal (Pb) has been prepared and the pH of sorbate solution was adjusted by adding HCl or NaOH. The effect of pH on adsorption process was studied by increasing pH of the solution 2 to 10 (initial metal concentration was 1000ppm).

The various results are shown in Table 3 and represented by figure 3. The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of Ionization and speciation of the adsorbate. The figure 3 shows the removal of the metal increased with increase in pH and reached maximum at pH 6 followed by a sharp increase in removal reaching close to 66 percent over the pH range 8.00 to 10.00. It can be explained as, according to stability constant calculations the increase of SO_4 the predominant species at $\text{pH} < 4.0$ is PbSO_4 . The formation of this has been found to decrease the Pb adsorption at this pH. The increase uptake of Pb ions at increased pH is due to the fact that at higher pH concentration of H^+ ion decrease, but the concentration of metal ions remains the same leading to increased uptake by adsorbent.

3.3 Effect of Adsorbent dose on Pb (II) uptake

The effect of adsorption dosage level on sorption of Pb(II) is shown in Table 4 and Figure 4. The study was carried out by taking 1000 ppm solution of metal. Adsorbent dose varied from 0.5gm/100ml to 4gm/100ml. More than 66.% of Pb removal occurs at dose level 4 gm/100 ml. So, like the other factors adsorption dose of adsorbent plays a vital role in the study of the percent removal of Pb(II). The higher dose of adsorbent due to an increased surface area, would have caused the availability of more number of adsorption sites resulting in higher uptake of metal ions.

3.4 Effect of initial metal concentration on metal uptake

The effect of initial concentration of metal ions on the sorption potential of adsorbent RHHP was investigated at pH 6.0 and the adsorbent dose 2.5g. The adsorption data of adsorbent at different initial concentrations of Pb(II) is shown in table 5 & 6. The adsorption increases with the increase in metal ion concentration, because the availability of more metal ions in the solution for adsorption.

3.5 Influence of temperature and study of adsorption Isotherm:

The Study on influence of temperature on metal sorption indicated the adsorption of Pb (II) on RHHP is exothermic the adsorption capacity decreased with an increase in the temperature of the system. This also proves the exothermic nature of the reaction. The two isotherms can be written as

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C_e$$

Freundlich adsorption isotherm and

$$\frac{1}{X/m} - \frac{1}{q_0} = \left(\frac{1}{q_0 b} \right) \frac{1}{C_e}$$

Langmuir adsorption isotherm

C_e is the equilibrium concentration (g/L) and X/m is the amount of metal adsorbed at equilibrium (g/g). q_0 and b are Langmuir constants respectively. q_0 signifies the adsorption capacity of the adsorbent and b is related to energy of adsorption process. A series of isotherm were determined at five different concentrations namely 50, 100, 150, 200, 250 mg/L, keeping all other experimental conditions constant. The values in the table 5 & 6 indicate that the uptake of metal ion per unit mass of the adsorbent increased with the increasing concentration of the solution. In Freundlich adsorption isotherm x/m is the amount of metals adsorbed per unit weight of adsorbent (g/g). C_e is the equilibrium concentration of sorbet K is a constant which is a measure of adsorption intensity. The liner plots of X/m Vs. $\log C_e$ (Fig - 5 and 7) suggest the applicability of the Freundlich model for Lead sorption. The values of Freundlich constants are given in table 7. The value of n (1 to 10) suggests the beneficial adsorption of

lead by RHHP. The Sorption data were also analyzed in the light of langmuir's model. The linear plots of $1/X_m$ versus $1/C_e$ (Fig – 6 and 8) suggest the applicability of the Langmuir model. The linear plots clearly indicate monolayer coverage of adsorbate at the outer surface of the sorbent. Langmuir constants and thermodynamic parameters calculated from the adsorption data are shown in Table 8. Standard molar or Gibbs free energy for these process is calculated as

$$\Delta G^0 = -RT \ln k$$

and the standard enthalpy change is calculated from the value of k at 293K and 313 K respectively.

$$\ln \frac{k_1}{k_2} = \frac{-\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

k_1 and k_2 are the respective constants at these temperature are derived from langmuir plots. Standard entropy change ΔS^0 for the process was calculated from the equation

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

From the data shown in table 8 for Pb(II) the value of q_0 (Langmuir Constant) decreases shows the exothermic nature of the adsorption. The value of ΔG^0 are negative which means that reactions are spontaneous. The magnitude of ΔG decreases with rise in temperature pointing towards spontaneity of the reaction and gradual change in affinity of metal ion by RHHP.

The value of enthalpy can be use to distinguish between chemical and physical adsorption of any adsorption process. The enthalpy values for Pb(II) comes to be -152.60 suggesting the exothermic nature of the process and physical sorption. Negative value ΔH^0 also suggests that the adsorption was energetically stable. The negative value of entropy of Pb(II) reflects the less affinity of adsorbent material (RHHP) for Pb(II) which also supported by the experiment results,

The essential characteristics of the langmuir equation can be described by a dimensionless equilibrium parameter R_L , which is defined by Hall et al

$$R_L = 1 / (1 + bC_0)$$

Where b is the Langmuir Constant (Lmg^{-1}) and C_0 is the initial metal ion (Pb Concentration (mgL^{-1})). The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), Linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). This study shows that shape of the isotherm is favorable i.e. R_L value $0 < R_L < 1$ (Table-9).

Table 1: Removal of Pb (II) by RHHP
Temp.- 293K pH = 6.0

S. No.	Weight of Adsorbent (gm)	Time Min.	Amount of Adsorbed ppm	% Removal of metal ion	Amount of Adsorbed (gm)
1	2.5	15	265.4	26.54	0.3450
2	2.5	30	335.0	33.50	0.4355
3	2.5	45	400.4	40.04	0.5205
4	2.5	60	535.4	53.54	0.6960
5	2.5	75	640.0	64.00	0.8320
6	2.5	90	690.6	69.06	0.8977
7	2.5	105	700.0	70.00	0.9100

RHHP = Rice Husk Hybrid Precursor

Table 2: Removal of Pb(II) by RHHP
Temp.- 313K pH = 6.0

S. No.	Weight of Adsorbent (gm)	Time Min.	Amount of Adsorbed ppm	% Removal of metal ion	Amount of Adsorbed (gm)
1	2.5	15	290.4	29.04	0.3775
2	2.5	30	370.0	37.00	0.4810
3	2.5	45	450.4	45.04	0.0585
4	2.5	60	510.0	51.00	0.6636
5	2.5	75	595.1	59.51	0.7736
6	2.5	90	640.0	64.00	0.8320
7	2.5	105	720.4	72.04	0.9365

Table 3: Percentage Adsorption of Pb (II)) by RHHP (Effect of p^H)

Temp.- 293K adsorbent weight- 2.5 gm Contact Time- 60 Min

S. No.	pH	Removed Amount of Pb(II) in ppm	Removed % Pb(II)
1	2	290.0	29.00
2	4	363.4	36.34
3	6	534.4	53.44
4	8	584.4	58.84
5	10	659.5	65.99

Table 4: Percentage Adsorption of Pb(II) by RHHP (Effect of adsorbent dose)

Temp.- 293K pH - 6.0 Contact Time- 60 Min

S.No.	Adsorbent dose gm/100ml	Removed Amount Of Pb (II) in ppm	Removed % Pb (II)
1	0.5	110	11.00
2	1.0	192.7	19.27
3	1.5	307.4	30.74
4	2.0	349.4	34.94
5	2.5	630.4	53.30
6	3.0	584.00	58.40
7	3.5	613.00	61.30
8	4.0	669.00	66.90

Table 5: Adsorption of Pb(II) On RHHP With Varying Metal Concentration
Temp.- 293K Adsorbent weight- 2.5 gm pH - 6.0 Contact Time- 60 Min

Initial Con. mg/L	Ce	X	X/m	Log Ce	Log X/m	1/Ce	1/X/m
50	1.01	48.99	0.019596	0.004321	-1.70863	0.99	51.03
100	6.9	93.1	0.03724	0.8388	-1.4289	0.1449	26.85
150	17.4	132.6	0.05304	1.2405	-1.2753	0.05747	18.85
200	36	174	0.0696	1.4149	-1.1573	0.03846	14.36
250	33	217	0.0868	1.5185	-1.06148	0.0303	11.52

Table 6: Values of Freundlich constants for Pb(II),

Metal Ion	log k		1/n		r (corr. coefficient)	
	293 K	313 K	293K	313 K	293K	313 K
Pb(II)	0.81	0.82	0.46	0.52	0.9868	0.9938

Table 7: Values of Langmuir Constants and thermodynamic parameters

Metal ion	q _o Value related to the equilibrium constant (L mole ⁻¹)		b (Lmg ⁻¹)		ΔG^0 (kJ mole ⁻¹)		Mean ΔH^0 (kJ mole ⁻¹)	Mean ΔS^0 (Jk ⁻¹ mole ⁻¹)
	293 K	313 K	293 K	313 K	293 K	313 K		
Pb	09	06	0.007	0.003	-52.82	-46.02	-152.60	0.346

Table 8: Equilibrium parameter, R_L calculated from Langmuir adsorption isotherm.

Metal ion concentration (mg/L)	Pb (II)	
	293 K	313 K
50	0.7407	0.8695
100	0.5882	0.7692
150	0.4878	0.6896
200	0.4166	0.6250
250	0.3636	0.5714

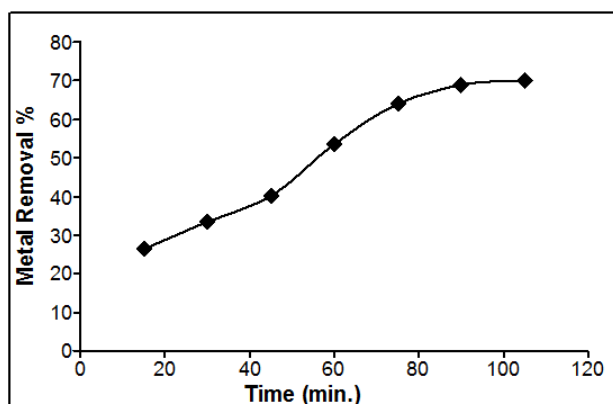


Figure 1: Effect of Contact time on adsorption of Pb (II) at 293K on RHHP

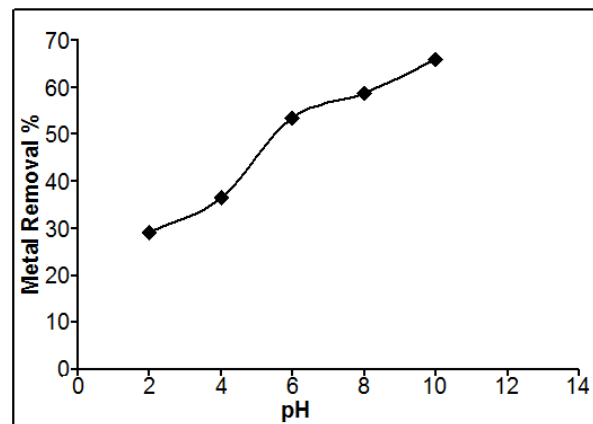


Figure 2: Effect of pH on adsorption of Pb (II) at 293K on RHHP

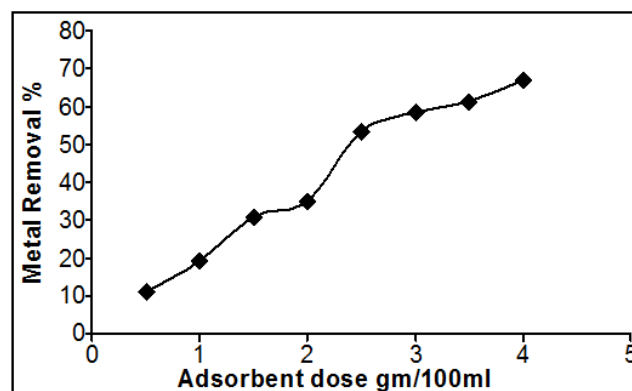


Figure 3: Effect of Adsorbent dose on adsorption of Pb (II) at 293K on RHHP

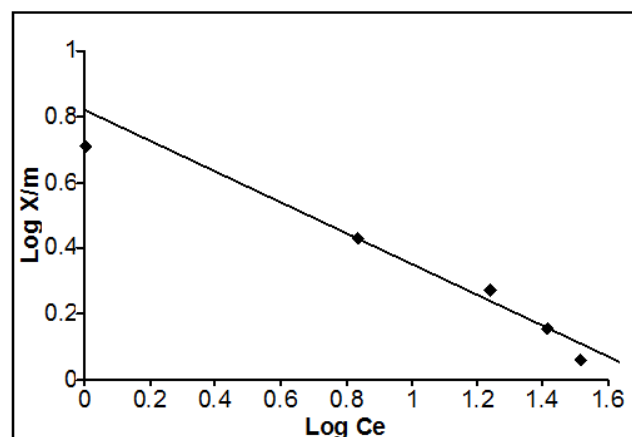


Figure 4: Freundlich adsorption Isotherm of Pb (II) at 293 K on RHHP

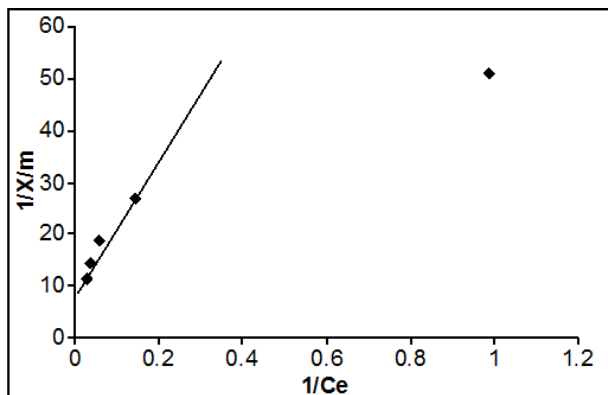


Figure 5: Langmuir adsorption Isotherm of Pb (II) at 293K on RHHP

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