



# Removal of lead from aqueous solution by hybrid precursor prepared by rice hull

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## ABSTRACT

Use of low-cost hybrid precursor, prepared from rice hull has been studied as a sorbent for the removal of  $Pb^{2+}$  from aqueous solutions. Effect of contact time, initial concentration, pH and temperature has been studied. The effect of temperature (30, 40, 50 and 60 °C) on adsorption phenomena has been studied and data have been analyzed using Langmuir isotherm. The change in enthalpy ( $\Delta H$ ) (–14.6179 kJ/mol), free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) has also been evaluated. The negative values of  $\Delta G$  and  $\Delta H$  indicate the adsorption of lead ions on the surface of hybrid precursor to be spontaneous and exothermic under the experimental condition.

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## 1. Introduction

Lead is highly toxic to human being. According to the US Environmental Protection Agency (EPA) [1], the permissible limit of lead in drinking water is 0.05 mg/L. Lead occurs in water in the divalent state and arises from a number of industrial and mining sources. Lead is widely used in storage battery [2], hot dip galvanizing, petroleum refining, printing and pigment industries, paints, paper and pulp, electrodes in electrochemistry and chemical industries [3,4,5]. About 5 million tons of the metal is produced annually all over the world [6]. The toxicity of lead has been extensively studied [1,2]. Lead is a cumulative poison and has a tendency to accumulate in blood, soft tissues and as lead tri-orthophosphate in bones [7,8]. It poses serious health hazards such as anemia and damage to kidney, lung, brain and central nervous system [9]. It has a half-life time of 25–40 days in blood and in soft tissues and more than 25 years in non-labial portion of bones [9].

For the separation of heavy metal ions such as lead ions from aqueous media, techniques like chemical precipitation, coagulation, complexions, ion exchange, solvent extraction, reverse osmosis, distillation and adsorption have been found to be effective [10]. However, these methods have several disadvantages that include incomplete metal removal, high reagent and energy

requirements and generation of toxic sludge or other waste products that requires proper disposal and further treatment. At low concentration, removal of pollutants is more effective by ion exchange or adsorption on solid adsorbents. However, high capital and regeneration cost of activated carbon and ion exchange resins have resulted in development of low-cost adsorbents. In wastewater treatment, the process of adsorption has an edge over other methods due to its sludge-free and colourless effluents. Among the various low-cost adsorbents reported for the removal of lead ions are tree bark, low-rank coal, human hair, peat mass, waste tire rubber, synthetic hydroxyl apatite [11], low-grade rock phosphate [12], clays and clay minerals [13–15], tea waste [16], talk [9], bituminous coal [17], seaweed [18], and clinoptilolite [19,20] etc. In the present study a hybrid precursor prepared using rice hull has been used as a low-cost adsorbent.

## 2. Experimental details

### 2.1. Materials and reagents

The rice hull in the present studies for making hybrid precursor of silicon and carbon was obtained from M/S Rice Mills, Bhopal, India. The rice hulls, after washing with distilled water was used for making sol, which was converted to hybrid precursor by alkaline hydrolysis at a pH of 8.0. The chemicals used were ethylene glycol (L.R. grade, S.D. fine chem. India), sodium hydroxide (A.R. grade, S.D. Fine Chem., India), ammonium nitrate (A.R. grade, S.D. Fine Chem., India) and lead nitrate (Merck A.R. grade).

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## 2.2. Synthesis of hybrid precursors

The preparation of hybrid precursor of silicon and carbon was carried out by refluxing 100 g of rice hull in 1000 mL solution of sodium hydroxide of different concentrations i.e. 3, 6, 9 and 12 M separately in the presence of 250 mL ethylene glycol. The refluxing of reactants was carried out for a period of 4 h in each experiment. The temperature of the reaction was (fixed) maintained at 198–200 °C. The reaction between various constituents resulted in the formation of sodium glycol/glycolato silicates mass. The excess quantity of (unreacted) ethylene glycol was recovered back by distillation. To prepare hybrid precursor, the sodium glycol/glycolato silicate mass so obtained was dissolved in 250 mL double distilled water. The pH of this solution was found to be 13–14. To this highly alkaline solution, 25% ammonium nitrate solution was slowly added under constant stirring at room temperature till the pH of the solution is reached to a value of 8.0. This led to the formation of hybrid precursor in the form of gel on allowing the solution undisturbed for duration of 24 h. The hybrid precursor gel was filtered using Whatman filter paper (No. 40) and dried at room temperature in air to preserve the gel matrix of hybrid precursor. The surface area of hybrid precursor was 97 m<sup>2</sup>/g as determined by Quanta chrome (Model – Nova-1000) BET surface area analyzer. Silicon and carbon content of hybrid precursor were estimated by wet chemical analysis method as per the procedure reported by Raman et al. [21]. The sodium content was estimated using flame photometer (Systronic model – Medi Flame). The results of the chemical analysis are reported in Table 1. From the results obtained, on the preparation of hybrid precursor it is found that the maximum percentage of silica could be extracted under optimum experimental conditions wherein 3 M sodium hydroxide solutions was used. Further it is also observed that the increases in concentration of alkali above 6 M reduce the extraction of silica from the rice hulls. Similar results have also been reported by Patel et al. [22]. Hence in the present study hybrid precursor prepared by 3 M sodium hydroxide was used. These hybrid materials e.g. carbon–silica gels also possess better adsorption properties than the values predicted by assuming additivity of properties of the individual components. For identification of various organic and other species present in the hybrid precursor, X-ray powder diffraction, <sup>29</sup>Si NMR, <sup>13</sup>C NMR, FTIR, TGA–DTA studies have been carried out. The results, which have been reported elsewhere, show that the major phases are glycolato silicate, sodium ammonium nitrate, hexa and nano hydrate sodium silicate, L-arabinose,  $\alpha$ -D-glucose.

## 2.3. Lead ion separation studies on hybrid precursor

For the studies on separation of lead ions using hybrid precursor, test solutions containing 5–500 mg/L lead ions were prepared in double distilled water by serial dilution of stock solution of 1000 mg/L lead nitrate. The stock solution was prepared by dissolving appropriate quantity of Analytical Reagent grade lead nitrate (Merck India make) in double distilled water and adjusting its pH to 6.0 by addition of dilute HNO<sub>3</sub>. The pH of the test as well as stock solution was adjusted with  $\pm 0.1$  pH accuracy using a digital pH meter and a combination glass electrode.

## 3. Results and discussion

### 3.1. Studies on optimization of contact time of adsorption

For optimization of contact time required for the sorptive separation of lead ions at hybrid precursor surface from aqueous solutions, hybrid precursor powder (0.5 g) was equilibrated with

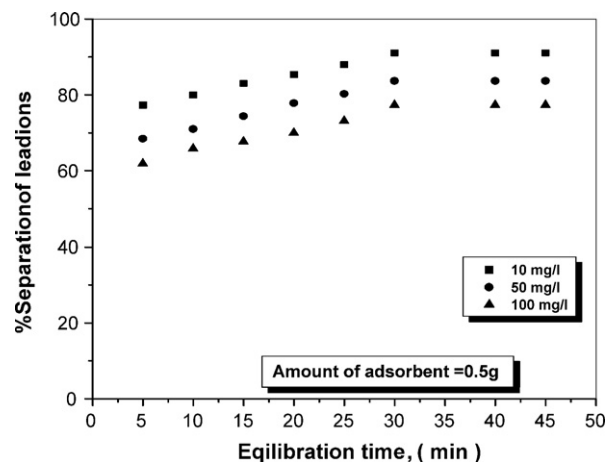


Fig. 1. Effect of contact time on percent sorption of lead ions on 0.5 g hybrid precursor from 100 mL test solution.

test solution (100 mL) containing lead ions (10, 50, 100 mg/L) for contact time of 5, 10, 15, 20, 25, 30, 40 and 45 min. The contact time comprises of 5 min stirring of the hybrid precursor powder with test solution using a mechanical shaker followed by equilibration for the remainder period under quiescent conditions. At the end of equilibration time, hybrid precursor was separated by filtration using Whatman filter paper (No. 42). The concentration of the remaining lead ions in solutions was estimated using Atomic Absorption Spectrometer (Shimadzu model Analyst-6300) following the procedure adapted earlier [23] to calculate the % separation of lead ions at different equilibration times. The results, which are given in Fig. 1 show that a contact time of 30 min is optimum.

### 3.2. Studies on optimization of quantity of adsorbent

For studying the effect of quantity of adsorbent on the % separation of lead ions, test solutions (100 mL) containing lead ions (10, 50, 100 mg/L) were equilibrated for 30 min at 20 °C with different quantities of hybrid precursor powder (0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2 and 3.4 g). The results are shown in Fig. 2. From the plots, it is inferred that equilibration of 0.5 g hybrid precursor is sufficient for removal of lead

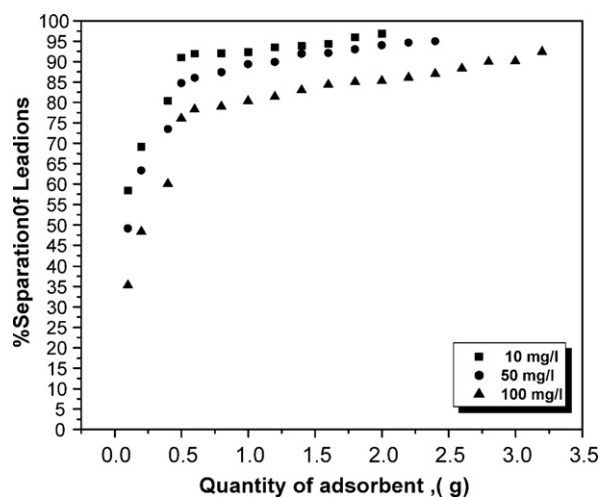
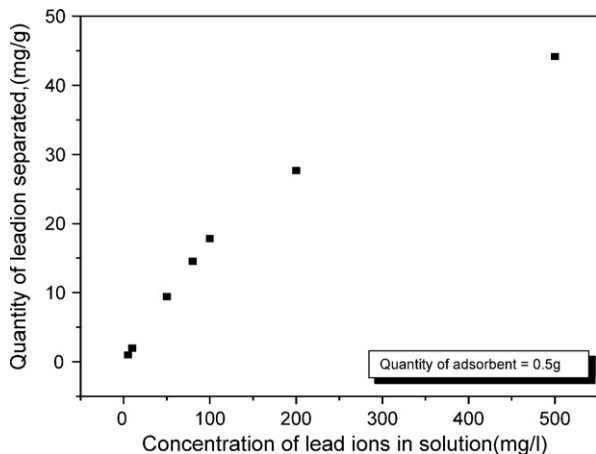


Fig. 2. Plot of percent separation of lead ions vs. quantity of adsorbent hybrid precursor from 100 mL test solutions of different concentrations of lead ions (given in inset) at 20 °C.

**Table 1**  
Results of synthesis experiments carried out for the preparation of hybrid precursor from rice hulls

Concentration of sodium hydroxide solution (M)	Yield of hybrid precursor (g/batch)	wt% <sup>a</sup> of various important constituents		
		Silica	Carbon	Sodium
3	60.43	27.60	16.41	0.21
6	65.64	26.33	20.12	0.56
9	70.51	24.28	22.52	0.64
12	70.55	20.12	24.65	0.72

<sup>a</sup> Calculated with respect to hybrid precursor and is average of 5–6 experiments for each batch.

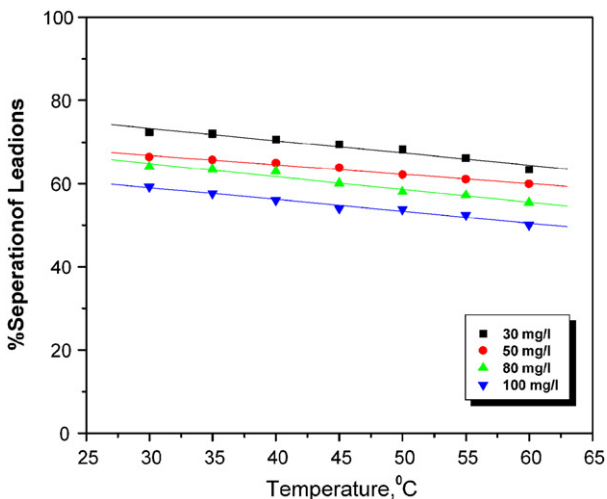


**Fig. 3.** Quantity (mg/g) of lead ion separated from 100 mL test solutions at 0.5 g hybrid precursor at 20 °C.

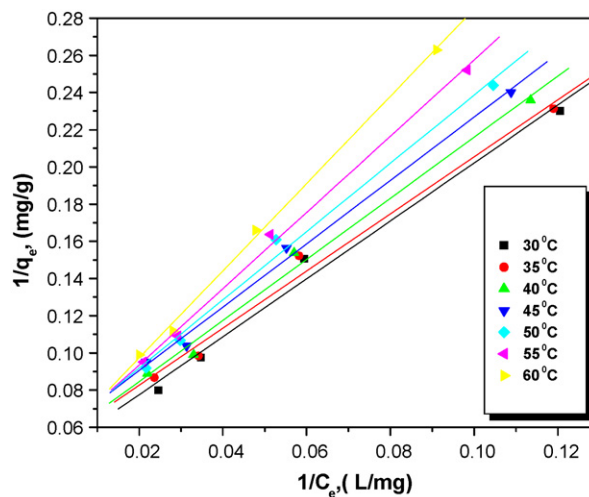
ions from 100 mL test solutions of different concentrations of lead ions.

**3.3. Studies on the effect of initial concentration of lead ions in solution on its %separation**

For studying the effect of initial concentration of lead ions in test solution on the %separation and quantity of lead ions separated per unit weight of adsorbent hybrid precursor (mg/g), 0.5 g of the adsorbent was equilibrated with test solutions containing 5, 10, 50, 80, 100, 200 and 500 mg/L lead ions at 20 °C for 30 min. The results of %separation and the quantity of lead ions separated (mg/g), which



**Fig. 4.** Effect of temperature on the quantity of separated lead ions per unit weight of adsorbent (mg/g) from 100 mL solution of different concentrations of lead ions (quantity of adsorbent used = 0.5 g).

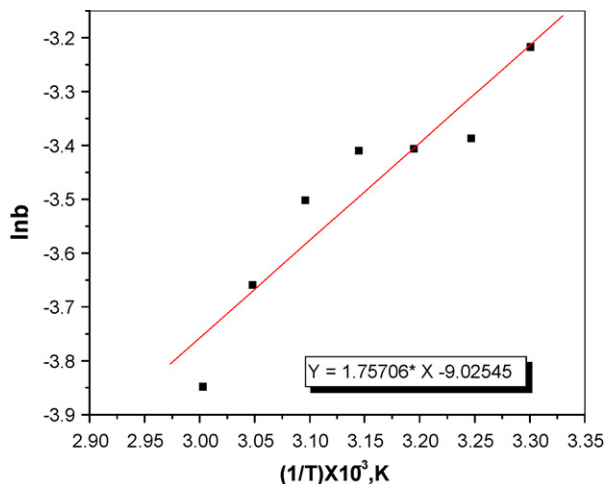


**Fig. 5.** Langmuir isotherm plot for the adsorption of lead ions at different temperatures.

can be calculated using Eq. (1) are shown in Fig. 3.

$$\text{Quantity of lead ions separated (mg/g)} = \frac{(C_o - C_e) \times 0.1}{\text{wt. of adsorbent in gm}} \tag{1}$$

The results show that the %adsorption is 95 from dilute solutions (5, 10 mg/L) but with the increase in concentration, the separation percentage decreases gradually to a value of ~50% in test solution containing 500 mg/L lead ions. The quantity of lead ions separated by hybrid precursor, initially increased rapidly with increase in the lead ion concentration in the solution but from solutions of higher



**Fig. 6.** Plot of ln b vs. 1/T for the adsorption of lead ions on the hybrid precursor surface.

**Table 2**  
Langmuir constants, thermodynamic parameters and linear regression constant for sorption of lead ions on hybrid precursor at different temperatures

Langmuir constants and thermodynamic parameters	Temperature (°C)						
	30	35	40	45	50	55	60
Langmuir constant $\theta^0$ , (mg/g)	21.645	19.260	19.294	17.656	18.089	18.964	19.801
Langmuir constant $b$ , (L/mg)	0.029	0.034	0.031	0.033	0.030	0.026	0.022
$\Delta G$ (kJ/mol)	-8.11	-8.68	-8.87	-9.02	-9.407	-9.98	-10.63
$\Delta S$ (J/mol)	2.14	1.92	1.836	1.759	1.613	1.412	1.119
$R^2$	0.993	0.987	0.995	0.994	0.996	0.996	0.999

concentrations (200 and 500 mg/L), the increase in the quantity of separated lead ions is low. This may be attributed to the effect that at low concentrations of lead ions in solution, surface coverage ( $\theta$ ) is small and hence almost all the available lead ions are removed. However, at higher concentrations the availability of sites for the adsorption reduces significantly. The quantity of lead ions separated per unit weight of adsorbent hybrid precursor (mg/g) is found to be 9.402 mg/g for 50 mg/L while with *Oryza sativa* L. husk it is 8.6 mg/g [24], however it is found 108 mg/g for 100 mg/L for tartaric acid modified rice husk. It is due the fact that the addition of carboxyl functional group enhances the sorption capacities of rice husk [25].

3.4. Studies on the effect of temperature on separation of lead ions

The sorptive separation of lead ions from 100 mL test solutions containing 30, 50 80, 100 mg/L lead ions was studied at 30, 35, 40, 45, 50, 55 and 60 °C. The percentage of separation of lead ions with 0.5 g hybrid precursor is observed to decrease with increase in temperature for all the concentrations of lead ions in test solutions studied, indicating exothermic nature of the sorption of lead ions on hybrid precursor (cf. Fig. 4).

3.4.1. Adsorption isotherms

The Langmuir adsorption isotherm indicates the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of solute remaining in the solution at equilibrium assuming the presence of a finite number of binding sites, homogeneously distributed over the adsorbent surface and presenting the same affinity for adsorption of a single layer, with no interaction between adsorbed species. The data obtained in the present studies for the adsorption of lead ions at hybrid precursor were analyzed using this isotherm, which is expressed as follows:

$$\frac{1}{q_e} = \left(\frac{1}{\theta^0 b}\right) \times \left(\frac{1}{C_e}\right) + \left(\frac{1}{\theta^0}\right) \tag{2}$$

where ‘ $q_e$ ’ is the amount of lead ions adsorbed per unit weight of adsorbent (mg/g), ‘ $C_e$ ’ is the equilibrium concentration of lead ions in test solution (mg/L), ‘ $\theta^0$ ’ is the adsorption capacity and ‘ $b$ ’ is the equilibrium constant of adsorption.

The dependence of  $(1/q_e)$  on  $(1/C_e)$  with varying concentration of lead ions in test solution at different temperatures is observed to be linear indicating the applicability of the Langmuir model to the adsorption of lead ions on hybrid precursor (cf. Fig. 5). From the values of slope and intercept, ‘ $\theta^0$ ’ and ‘ $b$ ’ were calculated for the isotherms obtained at 30, 35, 40, 45, 50, 55 and 60 °C and are given in Table 2.

The values of ‘ $b$ ’ so obtained were plotted against  $1/T$  (cf. Fig. 6) following Eq. (3)

$$\ln b = - \left(\frac{\Delta H}{RT}\right) + \text{constant} \tag{3}$$

The value of change in enthalpy was calculated from the slope of the straight line and was observed to be (-)14.6179 kJ/mol indicating the process to be exothermic in nature [26]. The change in free energy of the system due to adsorption at different temperatures of study was calculated using Eq. (4).

$$\ln b = - \left(\frac{\Delta G}{RT}\right) \tag{4}$$

As expected, the values of  $\Delta G$  obtained for different temperatures of study are observed to be negative indicates the spontaneous nature of the adsorption process. (cf. Table 2). The change in entropy of the system due to adsorption at different temperatures was calculated using Eq. (4):

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{5}$$

The value of entropy ( $\Delta S$ ) (cf. Table 1) at different temperatures has been defined as the degree of disorder of the system and positive values of this parameter as obtained in our investigation reflect the affinity of lead ions for the hybrid precursor.

The essential characteristics of isotherm are embodied in a separation factor which is dimensionless equilibrium parameter ‘ $R$ ’ [26,27] expressed as

$$R = \frac{1}{(1 + bC_0)} \tag{6}$$

Accordingly, values of  $R$  at different temperatures, calculated at different concentration of lead ions in test solution (cf. Table 3) were observed to be positive, lying between 0 and 1. Positive values of  $R$ , which are less than 1, confirm the favorability of the

**Table 3**  
Dimensionless equilibrium parameter, ( $R$ ); quantity (mg) of lead ion adsorbed/g of hybrid precursor

Temperature (°C)	Initial concentration of lead ions in solution (mg/L)							
	30		50		80		100	
	$R$	$q_e$	$R$	$q_e$	$R$	$q_e$	$R$	$q_e$
30	0.5289	4.34	0.4025	6.63	0.2963	10.24	0.252	11.86
35	0.457	4.31	0.372	6.56	0.270	10.16	0.228	11.53
40	0.5138	4.23	0.388	6.49	0.283	10.07	0.240	11.20
45	0.501	4.16	0.375	6.38	0.273	9.62	0.231	10.82
50	0.525	4.09	0.398	6.21	0.293	9.29	0.249	10.77
55	0.564	3.96	0.438	6.10	0.327	9.15	0.280	10.50
60	0.607	3.80	0.481	5.99	0.367	8.86	0.317	10.02

adsorption isotherm. The diagnostic criterion about the nature of isotherm involved, is as follows:  $R > 1$ , unfavorable isotherm;  $R = 1$ , linear isotherm;  $0 < R < 1$ , favorable isotherm and if  $R = 0$ , irreversible isotherm.

#### 4. Conclusions

The removal of lead ions from aqueous solution was carried out using hybrid precursor prepared from rice hulls. The separation of lead ions using hybrid precursor was observed to be significantly high (~95%) at lower concentration however with increase in lead concentration the separation gradually decreased to ~50%. The adsorption of lead ions on the hybrid precursor of in this study was observed to be (a) spontaneous, as evidenced by the negative values of Gibbs free energy ( $\Delta G$ ) and (b) exothermic as indicated from the observed negative values of enthalpy ( $\Delta H$ ).

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