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Removal of Lead from Aqueous Solutions Using Rice Husk

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ABSTRACT

Rice husk, an agricultural waste, was studied as a potential scavenger of lead from various aqueous solutions. Physicochemical parameters such as selection of appropriate electrolyte, shaking time, and the concentrations of adsorbent and adsorbate were studied to optimize the conditions to be utilized on a commercial scale for the decontamination of effluents using a batch technique. Maximum adsorption was observed with 0.01 mol·dm^{-3} acid solutions (HNO_3, HCl, H_2SO_4 and $HClO_4$) using 1000 mg of adsorbent for a 4.82×10^{-5} mol·dm^{-3} lead concentration in less than 10 minutes equilibration time. Studies show that the adsorption decreases with an increase in the concentrations of all the acids. The adsorption data follows the Freundlich isotherm over the 9.65×10^{-5} to 4.83×10^{-3} mol·dm^{-3} range of lead concentration. The characteristic Freundlich constants, i.e., $1/n = 0.93 \pm 0.04$ and $A = 19.86 \pm 0.82$ m·mol·g^{-1}, have been computed for the sorption system. Thermodynamic parameters, i.e., $\Delta G°$, $\Delta S°$, and $\Delta H°$, have also been calculated for the system.

INTRODUCTION

Lead as an environmental pollutant has drawn considerable concern because of its insidious effects on human beings and on the mental health of

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children in particular. The main sources of lead pollution include the use of tetramethyl- and tetraethyllead as gasoline additives; the manufacture of storage batteries; the formation of alloys with antimony and tin to be used in power and telephone cables; the manufacture of soldering material, lead paints, iron and steel, etc.

Various procedures are available for the preconcentration and removal of lead from effluents and polluted water. These include precipitation as sulfide (1), formation of volatile compounds such as hydride (2, 3) and alkylates (4), solvent extraction (5, 6), ion exchangers (7), ferritization (8), and adsorption. Adsorption of lead on various inorganic materials and organic compounds has been studied by various workers. The inorganic sorbents used for lead are geothite (9); oxides of silicon, manganese, and aluminum (10, 11); activated carbon (12); bentonite (13); hydrated titanium dioxide (14); and modified silica gel (15, 16). The organic sorbents for lead include polycarbonate filters (17), polyacrylonitrile and acrylonitrile charcoal composites (18), and polymethacrylic acid and poly(methyl methacrylate) (11). All these methods are effective for the removal of heavy metals from waste or polluted waters but are either time consuming or expensive, hence there is a need to look for more economical and effective methods for this purpose.

Many workers have used certain agricultural by-products such as peanut skin, onion skin, tree bark, maize cobs, and groundnut husk (19–23) for the removal of lead from industrial waste waters. The present work deals with a series of experiments to assess the utility of rice husk as an adsorbent for the removal of lead from aqueous solutions. As Pakistan is a major producer of rice (4.144 million tons annually), and husk accounts for about 20–23% of the whole rice, this material is abundantly available at no cost as waste material and contains 15–22% SiO_2 in a hydrated amorphous form like silica gel (24), which is one of the good adsorbents.

EXPERIMENTAL PROCEDURE

Equipment

Absorbance measurements were made with a Hitachi Model Z-8000 Polarized Zeeman atomic absorption spectrometer coupled with a microprocessor-based data-handling facility and a printer. A water-cooled, premix, fishtail-type burner with a 10 × 0.05 cm slot was used for the air-acetylene flame. A hollow cathode lamp of lead from Hitachi was used as the radiation source. All pH measurements were carried out with a digital pH meter-605 from Metrohm.

Reagents

A stock solution of lead (1000 $mg{\cdot}L^{-1}$) was prepared by dissolving 1 g of Specpure metal (Johnson & Mathey) in a minimum amount of distilled nitric acid (25). The resultant solution was diluted to 1 L with water. Standard solutions were prepared by appropriate dilution of this stock solution. Fresh working standards were made immediately before use. Glassware was cleaned by overnight soaking in nitric acid (1:1) followed by multiple rinses with water. Distilled and deionized water was used throughout.

The husk of basmati rice was obtained from a rice mill near Lahore. The husk was thoroughly washed with water to remove all dirt and was oven dried at 80°C to constant weight. The dried husk was stored in a precleaned airtight container and was used as such without any physical or chemical pretreatment.

Buffer solutions of 1 to 10 pH, with an ionic strength of 0.1 M, were prepared by using appropriate volumes of solutions of KCl and HCl (pH 1–3), CH_3COONa and CH_3COOH (pH 4–6), NH_4Cl and NH_4OH (pH 6–7.5), and H_3BO_3, NaCl, and NaOH (pH 8–10). All the reagents used were of Analytical Grade and were used as such.

Procedure

The adsorption of lead was carried out by a batch technique at room temperature (23 ± 1°C) except where otherwise specified. A known amount of rice husk (W) was taken in a 50-cm^3 glass vial with a screwed polyethylene cap and soaked in the acid or buffer in which the adsorption was to be carried out. After 5 minutes the excess solution was drained and a known volume of standard lead solution (V) was added along with 5 cm^3 acid or buffer. The contents were equilibrated on a mechanical shaker for 10 minutes and centrifuged for 3 minutes for phase separation. The concentration of lead in the liquid phase was determined before (C_i) and after (C_f) equilibration by flame atomic absorption spectrophotometry using the optimized instrumental conditions. A blank solution without metal was also prepared and treated under identical conditions. The signal evaluation was made by subtracting the blank from the absorbance of the sample. The following equations were used to compute the distribution ratio (K_d) and percentage sorption:

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \tag{1}$$

$$\%\ \text{Sorption} = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

RESULTS AND DISCUSSIONS

The adsorption of lead in aqueous solutions on rice husk was examined by optimizing various parameters such as the variable concentrations of min-

TABLE 1
Trace Element Concentration (μg/g) in Pakistani Rice Husk by INAA and AAS

Element	Range	Median
Hg	0.141–0.436	0.39
Cd[a]	28–140	34
Pb[b]	1.56–3.48	2.22
As	0.12–0.19	0.147
Sb	0.016–6.8	0.99
Ni	0.207–2.29	0.73
Se	0.125–0.176	0.15
Br	5.52–9.8	6.7
Al	75.5–122	92
Cs[a]	18–55	22
Fe	99–154	125
Cu	3.3–8.1	4.3
Zn	10.6–18.4	14.4
Mn	32.2–95.0	74.0
Cr[a]	188–465	312
Co[a]	73–197	114
V	0.56–1.20	0.65
Cl	1865–7373	2891
Na	109–586	204
K	2500–6200	5201
Rb	1.8–2.7	2.2
Sc[a]	14–44	27

[a] Concentration expressed in ng/g.
[b] Determined by AAS.

eral acids, the pH, equilibration time, and the amount of adsorbent and adsorbate using the atomic absorption spectrophotometric technique. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. The effect of temperature on the adsorption of lead was also checked. All the reported results are the average of at least triplicate measurements. The expected error is within ±3.0%.

The chemical analysis of 10 husk samples of basmati rice was carried out employing NAA and AAS techniques for their trace metal contents, and the results are summarized in Table 1. The silica contents of the rice husk were determined by the destruction of organic matter with an acid mixture of HNO_3 and $HClO_4$ (5:3) at 280°C in a Teflon beaker and then weighing the dry residue after washing it with water. The dry residue was then dissolved in HF solution at about 110°C. No residue was left behind, confirming the silica contents. The silica contents were found to be 17.97 ± 0.62%. The silica contents in the rice husk were also determined by x-ray fluorescence spectrometry using the standard addition method, and they were found to be 18.65 ± 0.63%. These determined values are in good agreement and are in the range of reported values of 15–22% (24).

Effect of Acid Concentration

The chemical treatment of metal oxide surfaces results in certain changes in surface properties. Therefore, the adsorption behavior of lead (4.82×10^{-5} mol/L) was measured in mineral acid solutions (HCl, HNO_3, H_2SO_4, and $HClO_4$) with concentrations ranging from 0.01 to 3.0 M. The results, reported in Figs. 1a and 1b, show significant decreases in the adsorption of lead with an increase in acid concentration from 0.01 to 3.0 M. This can be explained on the basis of a competitive reaction between H^+ ions in the medium and positively charged lead ions.

However, in the case of sulfuric acid an apparent increase in the adsorption of lead was observed beyond 0.5 M acid solutions, which may be due to the formation of insoluble lead sulfate which would result in less concentration of lead in the equilibrated solution.

The adsorption of metal ions on a hydrous oxide surface can probably be explained on the basis of the surface complex formation model. In this model the hydrolysis of silicon dioxide produces the hydrous oxide surface group —SiOH, i.e., the silanol group. This results in the formation of a weakly acidic silica surface with $K_a = 10^{-6}$ to 10^{-8} (26). The cation-exchange reaction can occur in aqueous solutions as follows:

$$m(\text{—SiOH}) \leftrightarrow m(\text{—SiO}^-) + m\text{H}^+ \tag{3}$$

$$\text{M}^{n+} + m(\text{—SiO}^-) \leftrightarrow \text{M(OSi—)}_m^{n-m} \tag{4}$$

The overall reaction can be represented as

$$\text{M}^{n+} + m(\text{—SiOH}) \leftrightarrow \text{M(OSi—)}_m^{n-m} + m\text{H}^+ \tag{5}$$

where M^{n+} = metal ion with an $n+$ charge
—SiOH = silanol group on SiO_2 surface
mH^+ = number of protons released

Reaction (5) is reversible in acid solution. In the present study the decrease in the adsorption of lead at a higher acid concentration can be explained on the basis of the competitive reaction of the protons and the metal ions. The maximum adsorption of metal at 0.01 M acid concentration is in accordance with the concept of zero point charge (ZPC) which lies in the 1.8–2.2 pH range for SiO_2 (27). This indicates that the adsorption of metal occurs on the surface of SiO_2 present in rice husk.

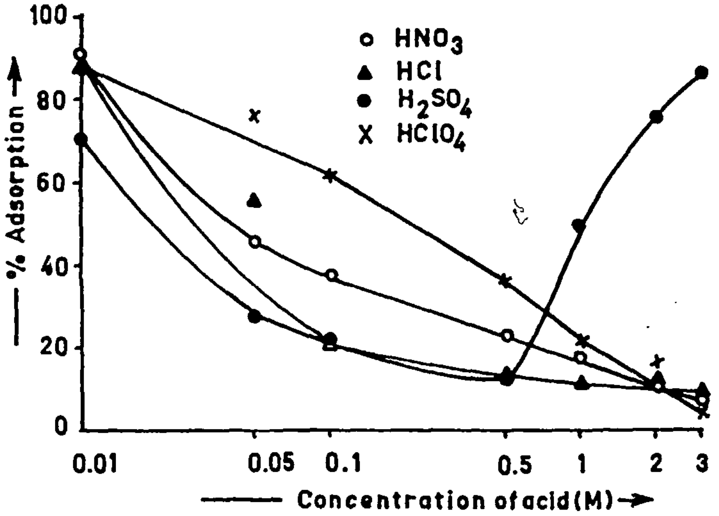

FIG. 1a Variation of percent adsorption of lead on rice husk as a function of acid concentration.

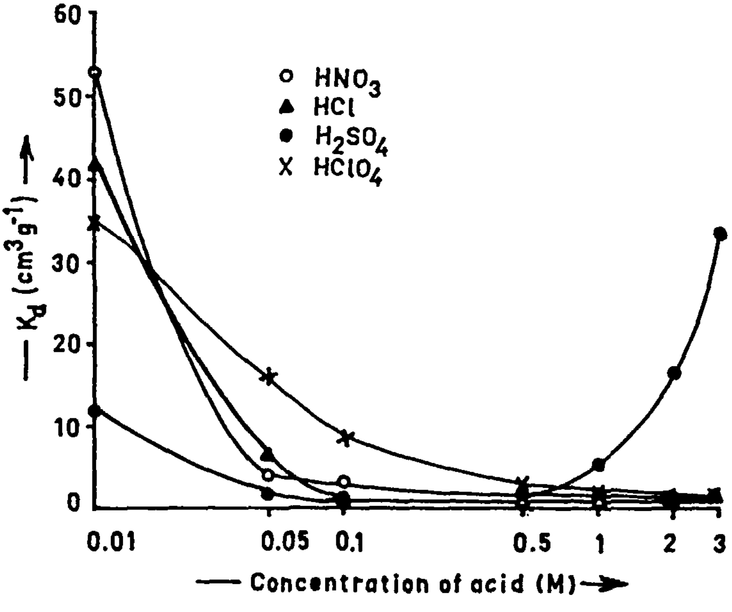

FIG. 1b Variation of K_d for the adsorption of lead on rice husk as a function of acid concentration.

Effect of pH

The removal of lead from wastewaters by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent, the degree of ionization, and the speciation of the adsorbate species. The adsorption of lead was therefore carried out from aqueous solutions of different pH values covering the range from 1 to 10, using 1.0 g of rice husk and a fixed amount of lead (2.41 × 10^{-5} mol/L). The results obtained are presented in Fig. 2. It was observed that the maximum adsorption of lead on rice husk occurred at pH 6, which gradually decreased with a further increase in pH. The adsorption at near-neutral pH could be attributed to the cellulose part of the rice husk, where site-binding adsorption might be occurring. This could probably be due to the surface complexation phenomenon which is facilitated by dissociation of the acidic functional groups (—COOH, —SH, etc.) present in the rice husk, which is essentially dependent upon their pK_a values. The pK_a values lie from 4.4 for aspartic and glutamic acid to 10.0 for lysine, which are three components of rice husk along with other constituents. Similar results have also been reported for the adsorption of lead on cellulose acetate membrane filters (17), a acrylonitrile–charcoal composite (18), and poly(methyl methacrylate) (11). The decrease in the adsorption of lead noted at alkaline pH is probably due to the formation of a hydroxide.

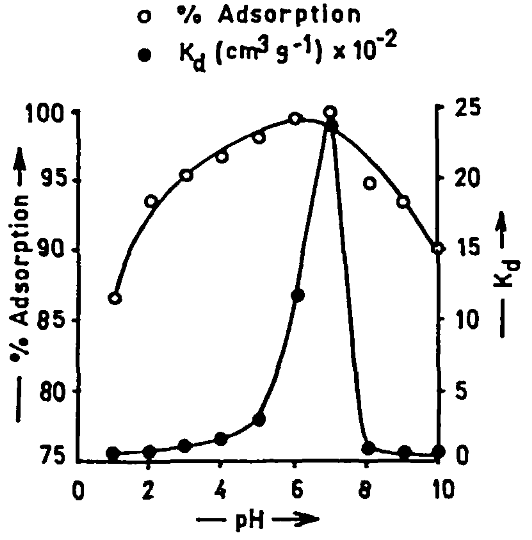

FIG. 2 Effect of pH on the adsorption of lead on rice husk.

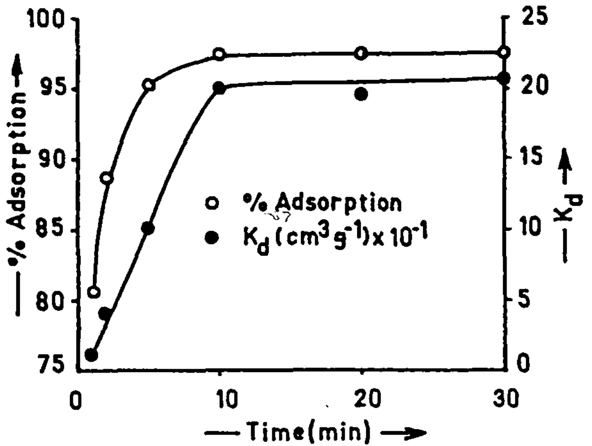

FIG. 3 Influence of equilibration time on the adsorption of lead on rice husk.

Effect of Shaking Time

The variation of percent adsorption of lead with shaking time was also studied using 5.0 cm^3 of 4.82 × 10^{-5} mol/L of lead solution in 0.01 M HNO_3 with 1.0 g of rice husk. The shaking time was varied from 0.5 to 30 minutes, and the results are shown in Fig. 3, which is a plot of percent adsorption of lead versus shaking time. It is seen that the percentage adsorption increases with an increase in shaking time. The maximum adsorption was observed at 10 minutes, beyond which there is no further increase in adsorption. Therefore, a shaking time of 10 minutes was considered to be sufficient for the adsorption of lead on rice husk and was used for all subsequent experiments.

Effect of Amount of Adsorbent

The amount of adsorbent also affects the efficiency of adsorption, and this parameter was also optimized by shaking 4.82 × 10^{-5} mol/L of lead solution using the optimized parameters. The amount of rice husk was varied from 0.2 to 2.0 g, and the results presented in Fig. 4 show that just 1.0 g of rice husk is sufficient for the quantitative removal of lead from the aqueous solution used. This amount of rice husk was used for further investigations.

Effect of Concentration of Adsorbate

The effect of lead concentration on the adsorption process was studied under the optimized conditions of shaking time, pH, and the amount of adsorbent. The concentration of lead was varied from 9.65×10^{-5} to 4.83×10^{-3} mol/L. The observed adsorption of lead was almost constant up to 3.86×10^{-3} mol/L of lead; beyond this concentration the adsorption decreased gradually with an increase in the concentration of lead. This can be explained in terms of the relatively smaller number of active sites at a higher concentration of lead. The loading capacity of rice husk was calculated and found to be 4.0 g lead per kg of rice husk.

The results of the lead concentration dependence study on rice husk were also subjected to analysis in terms of Langmuir and Freundlich adsorption isotherms. The data do not fit the Langmuir equation. However, the Freundlich adsorption isotherm was capable of describing the data over the entire concentration range studied. The Freundlich isotherm was tested in the following linearized form:

$$\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_e$$

where C_{ads} = amount of lead adsorbed ($\text{mol}\cdot\text{g}^{-1}$)
C_e = equilibrium concentration of lead in solution ($\text{mol}\cdot\text{L}^{-1}$)
A and $1/n$ = Freundlich constants

A plot of log C_{ads} versus log C_e yields a straight line. This linear plot (Fig.

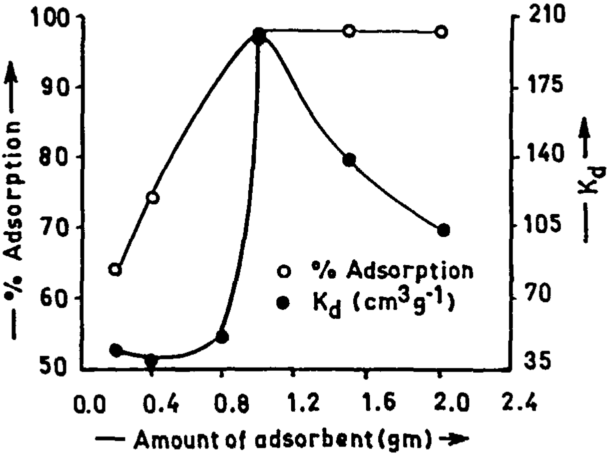

FIG. 4 Effect of amount of adsorbent on the adsorption of lead.

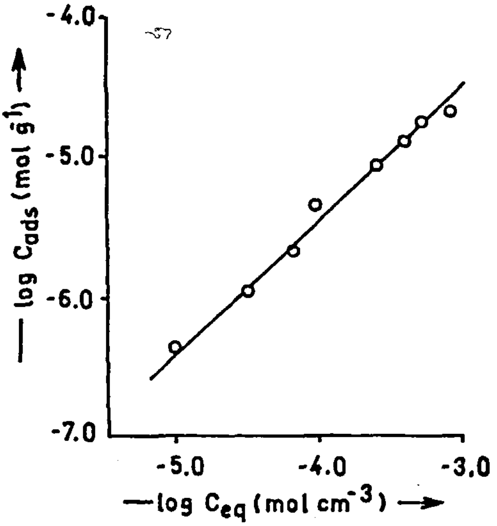

FIG. 5 Freundlich plot for the adsorption of lead on rice husk.

5) supports the applicability of the Freundlich adsorption isotherm in the present study. Similar results were reported for the adsorption of lead on poly(methyl methacrylate) (11).

The values of $1/n$ and A, which are rough measures of the adsorption intensity and adsorption capacity of the adsorbent, respectively, have been determined by a least-square fit program and were found to be $1/n = 0.93 \pm 0.04$ and $A = 19.86 \pm 0.82$ mmol·g^{-1}. The higher fractional value of $1/n$ signifies that strong adsorptive forces are operative on the surface of rice husk. Higher values of A further confirm the higher affinity of lead toward rice husk surface.

Effect of Temperature

The effect of temperature on the adsorption of lead on rice husk was also checked using the optimized conditions. The temperature was varied from 283 to 323 K. It was observed that the K_d value increases with an increase in temperature (Table 2), indicating better adsorption at higher temperature. The increase in the amount of lead adsorbed with an increase in temperature may be due either to acceleration of some slow adsorption steps or to creation of some new active sites on the adsorbent surface.

The values of $\Delta H°$ $\Delta S°$ were obtained from the slope and intercept of the Van't Hoff plot of ln K_d with the reciprocal temperature $1/T$ (Fig. 6) by using the relation

TABLE 2
Adsorption Studies of Lead on Rice Husk as a Function of Temperature

Rice husk	1000 mg
Shaking time	10 min.
Volume equilibriated	5 cm^3
Concentration of HNO$_3$	0.01 M
Concentration of lead	4.82×10^{-5} mol·L^{-1}

Temperature (K)	$1/T$ (K^{-1})	Concentration of lead (mol/L)	Concentration adsorbed per gram of adsorbent (mol/g)	K_d (cm^3·g^{-1})	ln K_d
283	3.533×10^{-3}	4.47×10^{-5}	1.78×10^{-8}	63.68	4.15
293	3.413×10^{-3}	4.53×10^{-5}	1.48×10^{-8}	78.33	4.36
303	3.300×10^{-3}	4.64×10^{-5}	9.30×10^{-9}	129.77	4.86
313	3.195×10^{-3}	4.61×10^{-5}	1.08×10^{-8}	109.67	4.69
323	3.096×10^{-3}	4.65×10^{-5}	6.30×10^{-9}	133.88	4.89

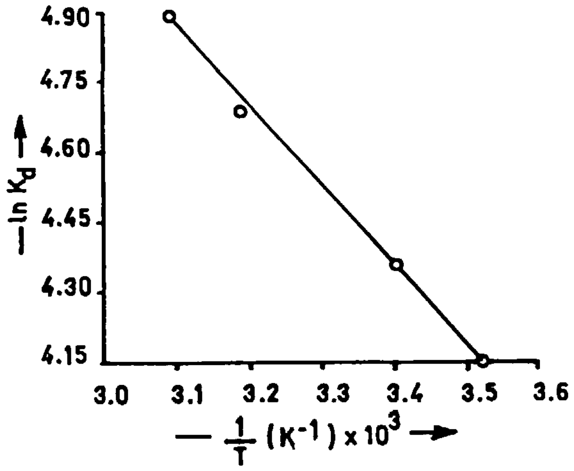

FIG. 6 Van't Hoff plot of the adsorption of lead on rice husk; ln K_d vs $1/T$.

TABLE 3
Thermodynamic Parameters for Lead Adsorption on Rice Husk

Temperature (K)	ΔG° (kJ·mol^{-1})	ΔH° (kJ·mol^{-1})	ΔS° (J·deg^{-1}·mol^{-1})
283	−9.765	13.772	83.170
293	−10.621		83.252
303	−12.243		85.858
313	−12.205		82.994
323	−13.132		83.294

$$\ln K_d = \frac{\Delta S^\circ}{T} - \frac{\Delta H^\circ}{RT}$$

where K_d = distribution coefficient (cm^3/g)
ΔS° = entropy change for the process
ΔH° = enthalpy change for the process
R = gas constant
T = absolute temperature

The free energy of specific adsorption, ΔG°, was calculated by using the equations

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

$$\Delta G^\circ = -RT \ln K_d$$

The ΔG° values obtained from these equations were in quite good agreement with each other. The thermodynamic parameters determined for the adsorption of lead on rice husk are given in Table 3.

The negative values of ΔG° indicate that the adsorption of lead on rice husk is a spontaneous process, whereas the positive value of enthalpy (ΔH°) confirms that the process is endothermic. The positive value of ΔS° suggests increased randomness at the solid-solution interface during the adsorption of lead. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system.

CONCLUSIONS

The natural material rice husk showed a good adsorption ability for lead from aqueous solutions. The reaction rate was fast, requiring only a short contact time. The reaction was found to be endothermic and to occur in the presence of a variety of anions, with maximum adsorption noted in the presence of 0.01 M HNO_3. The loading capacity of rice husk for lead under the optimal conditions was 4.0 g lead per kg rice husk. On the basis of this study it is concluded that the widely available natural product rice husk, which finds little utility in general, has good potential as a cheap and effective scavenger for lead present in industrial aqueous effluents and can be effectively utilized for waste management and environmental protection purposes. Apart from the removal of lead, the concept of the recovery of lead and of high purity silicon in controlled conditions can also be exploited.

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