

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Potential of Sawdust for the Decontamination of Lead from Aqueous Media

Nasir Khalid^a; Sohaila Rahman^a; Shujaat Ahmad^a

^a Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

To cite this Article Khalid, Nasir , Rahman, Sohaila and Ahmad, Shujaat(2005) 'Potential of Sawdust for the Decontamination of Lead from Aqueous Media', *Separation Science and Technology*, 40: 12, 2427 — 2443

To link to this Article: DOI: 10.1080/01496390500267467

URL: <http://dx.doi.org/10.1080/01496390500267467>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Potential of Sawdust for the Decontamination of Lead from Aqueous Media

Nasir Khalid, Sohaila Rahman, and Shujaat Ahmad

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

Abstract: The sorption of lead ions on sawdust has been exploited to evaluate its potential for the decontamination of lead ions from aqueous solutions. Various physico-chemical parameters such as selection of appropriate electrolyte, equilibration time, amount of adsorbent, concentration of adsorbate, effect of diverse ions and temperature were studied in order to simulate the best conditions in which this material can be used as an adsorbent. Maximum adsorption was observed at $0.005\text{ mol}\cdot\text{L}^{-1}$ acid solutions (HNO_3 , HCl , and HClO_4) using 0.2 g of adsorbent for $4.83 \times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$ lead concentration in 10 min equilibration time. Studies show that the adsorption of lead decreases with the increase in the concentrations of all the acids. The adsorption data follows the Freundlich isotherm over the lead concentration range of 2.41×10^{-5} to $4.83 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$. The characteristic Freundlich constants, i.e., $1/n = 0.49 \pm 0.02$ and $K = 0.142 \pm 0.0038\text{ m}\cdot\text{mol}\cdot\text{g}^{-1}$ have been computed for the sorption system. The sorption mean free energy from the Dubinin-Radushkevich isotherm is $11.26 \pm 0.31\text{ kJ mol}^{-1}$ indicating ion-exchange mechanism of chemisorption. The uptake of lead decreases with the rise in temperature (293–323 K). Thermodynamic quantities, i.e., ΔG , ΔS , and ΔH have also been calculated for the system. The sorption process was found to be exothermic. The proposed procedure was applied for the removal of lead from battery water samples.

Keywords: Adsorption, lead, removal, sawdust

Received 8 February 2005, Accepted 8 June 2005

Address correspondence to Nasir Khalid, Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan.
E-mail: nasirk@pinstech.org.pk

INTRODUCTION

Lead is one of the environmental pollutants due to its multiple serious health effects on human beings. Its presence in air, water, and food articles, even at trace levels, can pose health hazards to human life which have been well documented in literature (1–3). The main sources of lead pollution include the use of tetramethyl and tetraethyl lead as gasoline additives, manufacturing of storage batteries, formation of its antimony and tin alloys used in power and telephone cables, manufacturing of ammunition, soldering material, paints, iron and steel, and more. All these sources contribute in making the water toxic beyond 0.05 mg Pb L^{-1} , the permissible limit for human consumption. Keeping in view the gravity of the situation, particularly toxicity in children, has diverted the global attention toward understanding its behavior in ecosystem and metabolism for adopting measures for its efficient removal from such industrial and municipal waste effluents.

Removal/preconcentration of lead from various matrices has been achieved by different procedures such as coprecipitation (4, 5), formation of volatile compounds such as hydride (6), and alkylates (7), solvent extraction (8, 9), ion exchangers (10), ferritization (11), and adsorption. Various workers have studied adsorption of lead on various inorganic materials and organic compounds. Among the inorganic sorbents used for lead are oxides of silicon, manganese, aluminum, titanium (12–14), activated carbon (15), bentonite (16), and modified silica gel (17). The organic sorbents for lead include polycarbonate filters (18), polyacrylonitrile and acrylonitrile charcoal composite (19), and ion exchange resin (20). All these methods are effective for the removal of lead from the waste or polluted waters but are either time consuming or expensive; hence there is a need to look into other inexpensive rapid and effective methods for this purpose.

Present study deals with a series of experiments to assess the potentials of sawdust (SD) for the decontamination behavior/mechanism of lead from aqueous solutions. The main constituents of wood particles include cellulose, lignin, hemicellulose, tannins resins, which have been used as adsorbents for the treatment of waste stream from the textile industry (21). It is also the continuation of our studies regarding the exploitation of cheaper agricultural by-products for the decontamination of toxic metals from aqueous media (22–24).

EXPERIMENTAL PROCEDURE

Equipment

The absorption measurements were made with a Hitachi model 180/80 polarized Zeeman atomic absorption spectrophotometer coupled with a

microprocessor-based data-handling facility. The instrument has a strong magnetic field across the burner and graphite furnace, which provides a double-beam optical correction system based on the Zeeman effect. A water-cooled, premix, fish-tail type burner, having a $10 \times 0.05 \text{ cm}^2$ slot, was used for the air-acetylene flame. Hollow cathode lamp of lead from Hitachi was used as a radiation source.

Reagents

Stock solution of lead (1000 mg L^{-1}) was prepared by dissolving 0.1 g of specpure metal (Johnson and Matthey) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 cm^3 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 rinsing with water. Distilled and deionized water was used throughout.

Buffer solutions of pH 1 to 12, having ionic strength of 0.1 mol L^{-1} , 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 8–12). All pH measurements were made with a Metrohm 605 digital pH meter equipped with a combined glass/calomel electrode. All the reagents used were of analytical grade and were used as such.

The sawdust (SD) of cedar wood used was obtained from a local sawmill. The sample collected was thoroughly washed with deionized water and was oven dried at 80°C till constant weight. The dried material was stored in airtight polyethylene bottles and used as such without any further physical or chemical pretreatment.

Sorption Measurements

Known amount of sawdust was taken in a 35 cm^3 culture tube with a screwed polyethylene cap along with 10 cm^3 of standard acid solution. A fixed amount of stock solution was added. The contents were equilibrated on a mechanical shaker for a specific time and centrifuged at 5000 rpm for phase separation. The supernatant solution was withdrawn and the amount of lead was determined in the solutions before (C_i) and after (C_f) equilibrium by atomic absorption spectrophotometry using the optimized instrumental parameters. A blank solution without metal was also prepared and treated similarly. All experiments were conducted at room temperature ($296 \pm 1 \text{ K}$) unless otherwise specified.

TREATMENT OF DATA

Adsorption of Metal

The percentage sorption of metal ion "M" from the solution was calculated using the following relationship:

$$\% \text{ Sorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

The distribution coefficient (K_d) was calculated from the equation

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \quad (2)$$

where

C_i = initial concentration of metal in the solution

C_f = concentration of metal in solution after equilibrium

V = volume of adsorbate solution (cm^3)

m = amount of adsorbent (g)

Calculation of Thermodynamic Parameters

Thermodynamic parameters were calculated using the following relations:

$$K_c = \frac{C_{ad}}{C_e} \quad (3)$$

If F_e is the fractional attainment of adsorption at equilibrium, then

$$C_e = C_i (1 - F_e) \quad (4)$$

$$\text{and} \quad C_{ad} = C_i F_e \quad (5)$$

where

K_c = equilibrium constant

C_e = equilibrium concentration of metal in solution (mg L^{-1})

C_i = initial concentration of metal in solution (mg L^{-1})

C_{ad} = equilibrium concentration of metal on the adsorbent (mg L^{-1})

By substituting the values of C_e and C_{ad} from Eqs. (4) and (5) into Eq. (3) K_c becomes

$$K_c = \frac{F_e}{(1 - F_e)} \quad (6)$$

which shows that the equilibrium constant is independent of the amount of adsorbent and of the volume of the solution.

The values of ΔH and ΔS were calculated from the slope and intercept of the linear van't Hoff plot, respectively, using the relation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where

ΔS = entropy change for the process

ΔH = enthalpy change for the process

R = gas constant

T = absolute temperature

The changes in standard free energy (ΔG) and entropy (ΔS) for the specific adsorption have also been calculated using the equations:

$$\Delta G = -RT \ln K_c \quad (8)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

where the symbols have their usual significance.

RESULTS AND DISCUSSION

The adsorption of lead ions from aqueous solutions on sawdust was examined by optimizing specified physicochemical parameters such as variable concentrations of mineral acids, equilibration time, amount of adsorbent and concentration of adsorbate, using batch method and employing atomic absorption spectrophotometry. 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 independent measurements. The expected error is within $\pm 3.2\%$ unless otherwise specified.

Effect of Acid Concentration

Interaction of various chemical compounds and electrolytes may alter the surface properties of the adsorbent, therefore, the adsorption behavior of lead ($4.826 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) was checked in mineral acid solutions (HNO_3 , HCl , and HClO_4) having a concentration range from 0.005 to 2.0 M using 0.2 g of SD. Sulphuric acid was not included in this study since it forms insoluble lead sulphate. The results presented in Figs. 1(a) and 1(b) show that maximum adsorption of lead ions was observed at 0.005 M acid concentration which then decreases with an increase in acid concentration

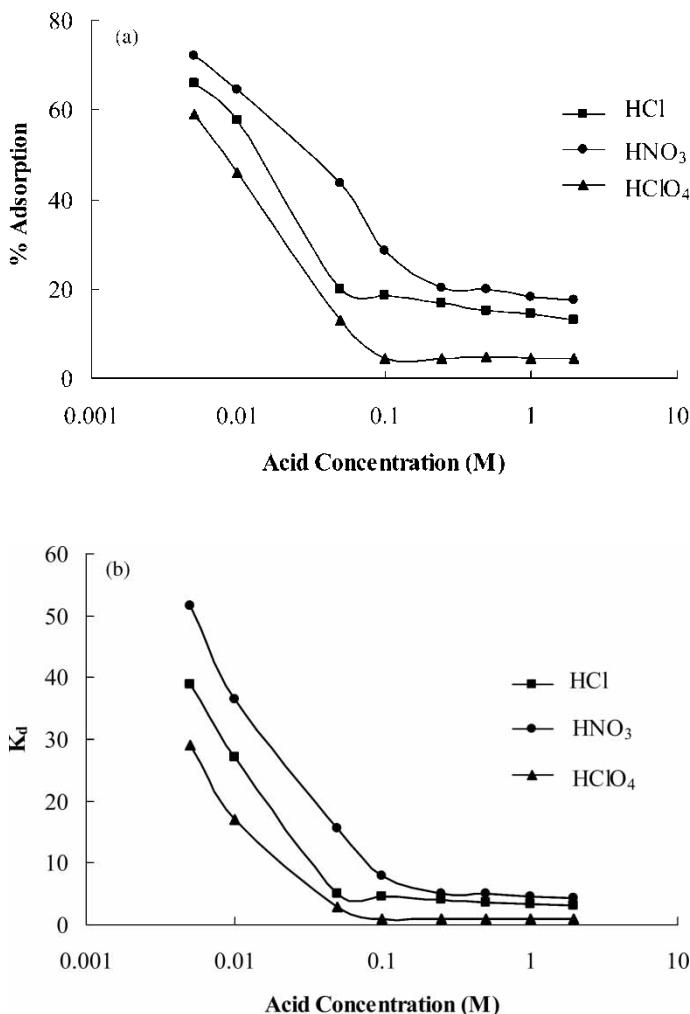


Figure 1. (a) Variation of percent adsorption of lead on sawdust as a function of acid concentration; (b) variation of K_d for the adsorption of lead on sawdust as a function of acid concentration.

from 0.005 to 2.0 M. Similar trends have been reported for the adsorption of lead on rice husk (22) and mercury on sawdust (25). The decrease in adsorption of lead with an increase in acid concentration may be attributed to the competition between the excess of H^+ ions in the medium and positively charged hydrolyzed species present in the solution. Also, a higher acid concentration appears to suppress hydrolysis of the element in hydrolyzed species, resulting in lower adsorption. It was also observed that maximum adsorption of lead occurred in 0.005 M HNO_3 as compared to the other

acids, therefore, this concentration of HNO_3 was used for all the subsequent experiments regarding the optimization of conditions for the adsorption of lead on SD.

Variation of pH

The removal of lead from aqueous solutions by adsorption is highly dependent on pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species. Such study helps in indicating the appropriate pH of the effluent/waste water for achieving maximum efficiency in the removal of metal ions by an adsorbent. The pH dependence study of lead adsorption on SD was, therefore, carried out from aqueous solutions of different pH covering a range of 1 to 12, using 0.5 g of adsorbent and fixed amount of lead ($4.83 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$). The results obtained are shown in Fig. 2. The percent adsorption increases with an increase in pH of the solution, and was maximum at pH 8. With further increase in pH the adsorption starts decreasing probably due to the formation of hydroxide of lead. Similar trend has been reported for the adsorption of mercury on sawdust (25). The low adsorption at lower pH could probably be due to the competition between H^+ ions and lead ions for a fixed number of adsorption sites. The maximum adsorption at pH 8 could be due to cellulose where site-binding sorption takes place.

The adsorption of metal ions on the surface of sawdust can probably be explained on the basis of the surface complex formation model, which is facilitated by the dissociation of carboxylic acid group in corillagin species, $\text{C}_{27}\text{H}_{24}\text{O}_{18}$, present in wood tannins, which results in the formation of metal

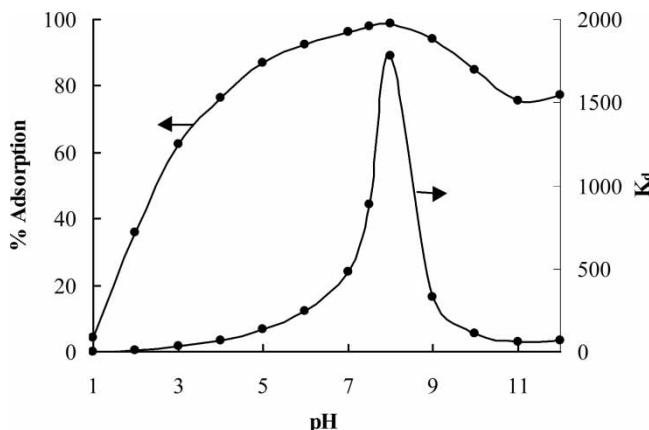
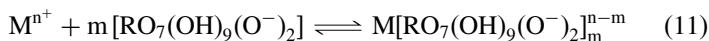
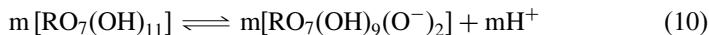
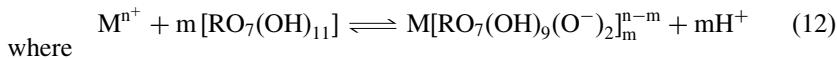


Figure 2. Effect of pH on the adsorption of lead on sawdust.

complex. The cation exchange reaction can occur in aqueous solutions as follows:



The overall reaction can be represented as:



M^{n+} = metal ion with $n+$ charge

$-RO_7(OH)_{11}$ = acidic part of wood surface

mH^+ = number of protons released

The reaction (12) is reversible in acid solution. In the present study the decrease in the adsorption of lead at higher acid concentration can be explained on the basis of competitive reaction of the protons in the medium and positively charged lead ions.

The enhanced adsorption of lead ions with an increase in pH could probably be due to the condensation reaction between the hydrolysis product of the sorbate ions and the sorbent carrying $-OH$ groups (26). It can, therefore, be concluded that the overall adsorption of lead ions on the surface of SD used is mainly due to the combined effect of site binding sorption and surface complexation phenomena.

Influence of Equilibration Time

The time dependence adsorption of lead on SD was studied using 10.0 cm^3 of $4.83 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$ of lead solution in $0.005\text{ mol} \cdot \text{L}^{-1}$ of HNO_3 with 0.5 g of sawdust. The equilibration time was varied from $0.5\text{--}20\text{ min}$ and results have been shown in Fig. 3. It is seen that the percentage adsorption increases with the increase in equilibration time. Maximum adsorption was observed at 10 min time, beyond which there is no further increase in the adsorption. Therefore, 10 min equilibration time was considered to be sufficient for the adsorption of lead on sawdust and was employed for all the subsequent experiments. The short equilibration time suggests that the adsorption process is a surface phenomenon proceeding between the metal ions and sorbent carrying $-COOH$ and $-OH$ groups.

Effect of Amount of Adsorbent

The influence of the amount of adsorbent on the adsorption efficiency was also studied by shaking 10 cm^3 of $4.83 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$ of lead solution using the

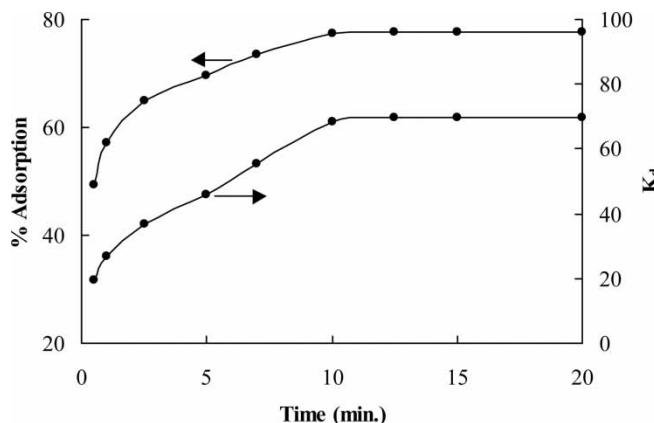


Figure 3. Influence of equilibration time on the adsorption of lead on sawdust.

optimized parameters. The amount of sawdust was varied from 0.10 to 2.0 g and the results have been represented in Fig. 4, which depicts that 1.0 g of sawdust is sufficient for the quantitative removal of lead from the aqueous solution used.

Variation of Adsorbate Concentration

Concentration dependence of lead adsorption on sawdust was studied under the optimized conditions of acid concentration, equilibration time, and the amount of adsorbent. The initial sorptive concentration of lead was varied from 2.41×10^{-6} to 9.65×10^{-4} mol \cdot L $^{-1}$ and the results are shown in Fig. 5, which indicates that the percentage adsorption decreases with the

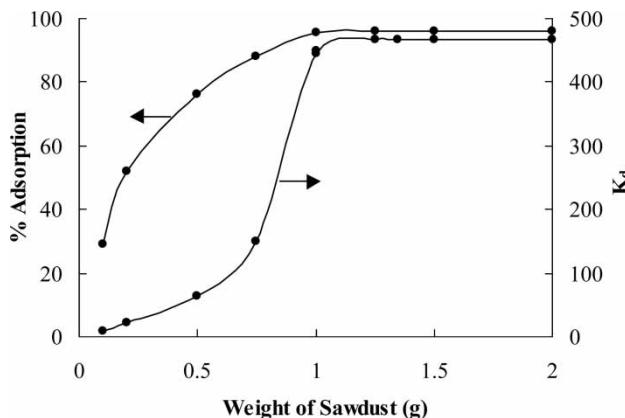


Figure 4. Effect of amount of adsorbent on the adsorption of lead on sawdust.

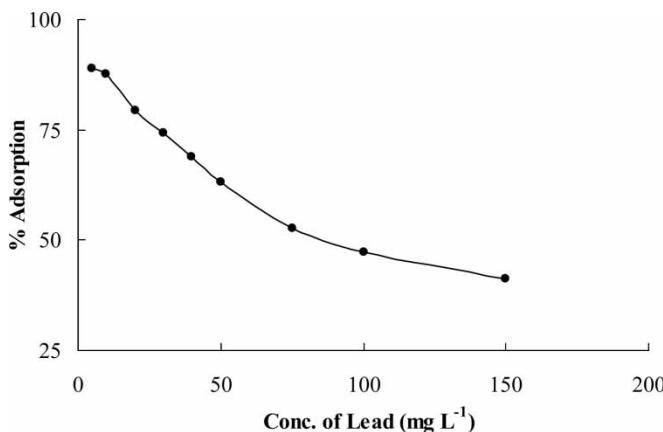


Figure 5. Adsorption variation of lead ion concentration.

increase in lead ion concentration. This can be explained in terms of relatively fewer numbers of active sites at higher concentration of lead.

The data for the adsorption of lead on sawdust has been analyzed in terms of the Freundlich mode of adsorption. It was found that the Freundlich adsorption isotherm was capable of describing the data in the concentration range of 2.41×10^{-6} to 4.83×10^{-4} mol \cdot L $^{-1}$. The Freundlich isotherm was tested in the following linearized form:

$$\log C_{ad} = \log K + 1/n \log C_e \quad (13)$$

where

C_{ad} = amount of lead adsorbed at equilibrium (mol \cdot g $^{-1}$)

C_e = equilibrium concentration of lead in solution (mol \cdot L $^{-1}$)

K and $1/n$ = Freundlich constants

A plot of $\log C_{ad}$ vs. $\log C_e$ yields a straight line (Fig. 6). This linear plot supports the applicability of the Freundlich isotherm model in the present study. Similar trend has been reported for the adsorption of mercury on sawdust (25). The values of Freundlich constants $1/n$ and K give a measure of the adsorption intensity and capacity of the adsorbent, respectively. These constants were evaluated from the slope and the intercept of the straight line (Fig. 6) using a least-square fit program and were found to be 0.49 ± 0.02 and 0.14 ± 0.0038 m mol \cdot g $^{-1}$, respectively. The fractional value of $1/n$ ($0 < 1/n < 1$) signifies that the surface of the sawdust is heterogeneous in nature (26).

To classify the physical or chemical adsorption, the data were applied to Dubinin-Radushkevich (D-R) isotherm model. The D-R equation is

$$C_{ad} = C_m \exp(-\beta \varepsilon^2) \quad (14)$$

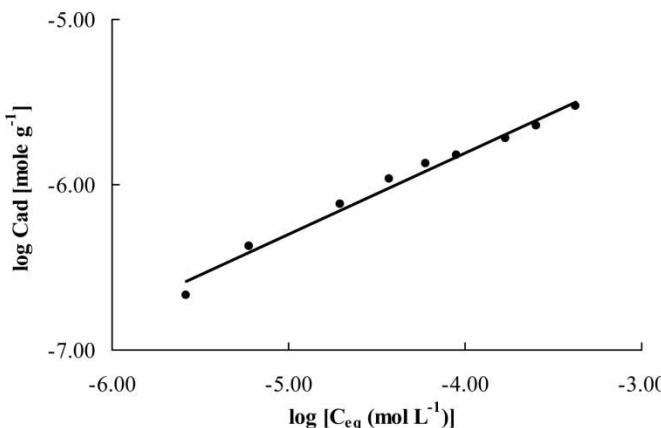


Figure 6. Freundlich adsorption isotherm of lead on sawdust.

where C_{ad} is the amount of lead adsorbed on SD, C_m is the maximum amount of lead that can be adsorbed on SD under the optimized experimental conditions, β is a constant with a dimension of energy, and ε (Polyanyi potential) = $RT \ln(1 + 1/C_e)$, where R is the gas constant in $\text{kJ mol}^{-1} \text{K}^{-1}$, T is the absolute temperature in K, and C_e is the equilibrium concentration of lead in solution. The linearized form of D-R isotherm is

$$\ln C_{ad} = \ln C_m - \beta \varepsilon^2 \quad (15)$$

when $\ln C_{ad}$ is plotted against ε^2 , a straight line was observed (Fig. 7). The computed values of β from the slope of this straight line was $-3.94 \times 10^{-3} \pm 1.08 \times 10^{-4} \text{ kJ mol}^{-2}$. From the calculated value of β the mean sorption energy (E) was computed as

$$E = \frac{1}{\sqrt{-2\beta}} \quad (16)$$

which is the free energy of transfer of one mole of solute from infinity to the surface of SD. The numerical value of E evaluated from equation (16) is $11.26 \pm 0.31 \text{ kJ mol}^{-1}$, which is in the expected range of $8\text{--}16 \text{ kJ mol}^{-1}$ for chemisorption or ion exchange (27).

Effect of Diverse Ions

The presence of other cations and anions in the adsorptive medium may change the environment and solution chemistry of the metal of interest, which effects the adsorption efficiency of an adsorbent. Therefore, using the optimized parameters the adsorption of $4.83 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of lead ions on sawdust was also studied in the presence of high concentrations of

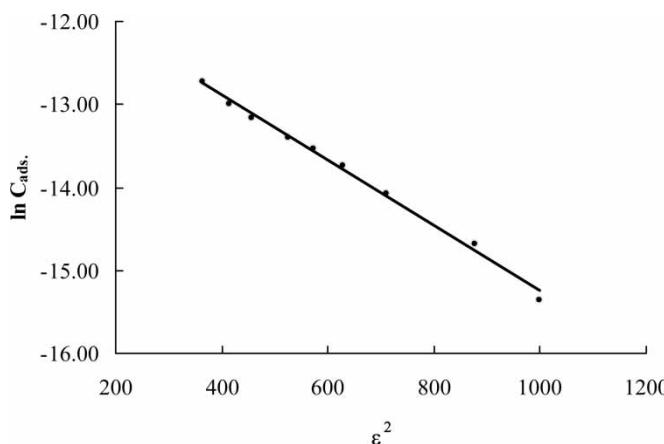


Figure 7. Dubinin-Radushkevich adsorption isotherm of lead on sawdust.

various cations and anions. The results are shown in Tables 1 and 2. All the anions were used as their sodium salts, whereas for cations the nitrate salts were used. The perusal of the data shows that the adsorption of lead on sawdust was almost quantitative in the presence of all the ions studied except EDTA, which masked the adsorption completely. Similarly the adsorption of lead on sawdust is significantly affected (up to 50%) in the presence of Ni, Mg, Mn, Fe, and Cu ions. This decrease in the adsorption of lead is probably due to the formation of stable complexes with chelating agent used and the utilization of the adsorption sites on the surface of sawdust by cations used.

Table 1. Effect of anions on the adsorption of lead ions on sawdust

Ions	Concentration (mol · L ⁻¹)	K _d	Adsorption (%)
None	—	192.0	96.0
NO ₃ [—]	5.0 × 10 ^{—3}	187.1	95.9
ClO ₄ [—]	5.0 × 10 ^{—3}	41.1	83.7
SO ₄ ^{2—}	5.0 × 10 ^{—3}	100.1	92.6
Cl [—]	5.0 × 10 ^{—3}	83.9	91.3
Br [—]	6.257 × 10 ^{—3}	42.6	84.2
I [—]	3.940 × 10 ^{—3}	119	93.7
Cit.	2.191 × 10 ^{—3}	125.3	94.0
CH ₃ COO [—]	8.466 × 10 ^{—3}	152.0	95.0
NO ₂ [—]	10.868 × 10 ^{—3}	60.4	88.3
EDTA	1.699 × 10 ^{—3}	1.3	14.0

Table 2. Effect of cations on the adsorption of lead ions on sawdust

Ions	Concentration (mol · L ⁻¹)	K _d	Adsorption (%)
None	—	192.0	96.0
Cd ²⁺	0.889 × 10 ⁻³	61.0	88.4
Cr ³⁺	1.923 × 10 ⁻³	187.1	95.9
Cu ²⁺	1.574 × 10 ⁻³	8.0	50.1
Ni ²⁺	1.703 × 10 ⁻³	7.1	47.1
Mn ²⁺	1.668 × 10 ⁻³	22.1	73.4
Fe ³⁺	1.791 × 10 ⁻³	3.5	30.5
K ⁺	2.558 × 10 ⁻³	95.9	92.3
Na ⁺	4.349 × 10 ⁻³	87.2	91.6
Ca ²⁺	2.495 × 10 ⁻³	68.9	89.6
Mg ²⁺	4.114 × 10 ⁻³	28.5	78.1

Effect of Temperature

The effect of temperature on the adsorption of lead ions (4.83×10^{-5} mol · L⁻¹) on sawdust was also checked using 0.5 g of adsorbent and other optimized conditions. The temperature was varied from 293 to 323 K. The amounts of lead ion adsorbed at various temperatures are shown in Table 3, which reveals that the uptake of lead decreases with the rise in temperature, indicating better adsorption at lower temperature. Similar results have also been reported for the adsorption of copper on cellulose (21).

The amounts of lead adsorbed at equilibrium at different temperatures have been utilized to evaluate the thermodynamical parameters for the sorption system. The van't Hoff plot of $\ln K_c$ vs. $1/T$ was a straight line (Fig. 8). The slope and intercept of this line were equal to $(-\Delta H/R)$ and $(\Delta S/R)$,

Table 3. Adsorption studies of lead ions on sawdust as a function of temperature

Temp. (K)	1/T (K ⁻¹)	Concentration	Concentration	K _c	$\ln K_c$
		adsorbed (mol · L ⁻¹)	in bulk (mol · L ⁻¹)		
293	3.413×10^{-3}	3.745×10^{-5}	1.081×10^{-5}	3.464	1.242
298	3.356×10^{-3}	3.591×10^{-5}	1.235×10^{-5}	2.906	1.067
303	3.300×10^{-3}	3.292×10^{-5}	1.535×10^{-5}	2.145	0.763
313	3.195×10^{-3}	3.002×10^{-5}	1.824×10^{-5}	1.645	0.498
323	3.096×10^{-3}	2.751×10^{-5}	2.075×10^{-5}	1.325	0.282

Sawdust: 500 mg; Shaking time: 10 min; Volume equilibrated: 10 cm³; Concentration of HNO₃: 0.005 mol · L⁻¹; Concentration of lead: 4.83×10^{-5} mol · L⁻¹.

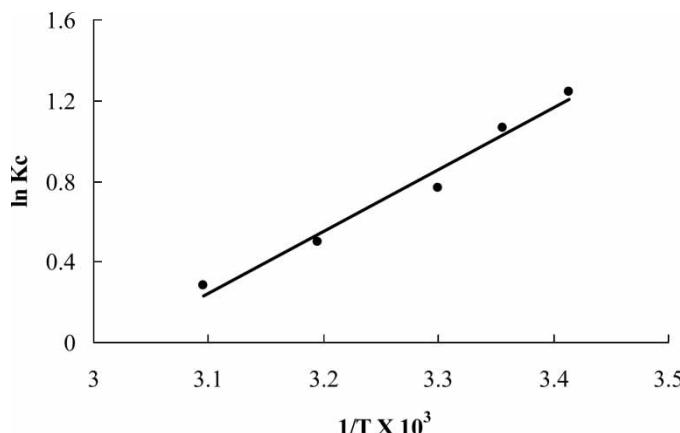


Figure 8. Van't Hoff plot for the adsorption of lead on sawdust.

respectively, thus allowing us to calculate ΔH and ΔS . By using Eq. (7) the estimated ΔH value for the present system was $-25.49 \text{ kJ mol}^{-1}$ (Table 4). The values of free energy of specific adsorption, ΔG , and entropy ΔS at various temperatures were calculated by using Eqs. (8) and (9) and have been listed in Table 4. The negative values of ΔG indicate that the adsorption of lead on sawdust occurs via spontaneous process. The decrease in the numerical value of $-\Delta G$ with the rise in temperature indicates that the sorption process of lead ions on sawdust is more favorable at lower temperatures. The negative value of enthalpy change (ΔH) confirms the exothermic adsorption of lead on sawdust. The negative value of ΔS suggests the decreased randomness at the solid-solution interface during the adsorption of lead on SD.

Application of the Procedure

In order to check the applicability of the developed procedure on some real samples, the uptake of lead ions from two battery water samples on sawdust

Table 4. Thermodynamic parameters for adsorption of lead ions on sawdust

Temperature (K)	ΔG ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔS ($\text{JK}^{-1} \cdot \text{mol}^{-1}$)
293	-3.03	-25.49	-76.67
298	-2.64		-76.67
303	-1.92		-77.78
313	-1.30		-77.30
323	-0.76		-76.58

Table 5. Determined composition of battery water samples

Cations/anions	Concentration (mg/L)	
	B1	B2
Ca	22.60	28.20
Mg	35.30	33.69
Na	85.60	156.30
K	5.80	10.37
Fe	0.22	0.31
Mn	0.02	0.05
Zn	0.18	0.21
Cu	0.01	0.02
Cd ^a	10.00	8.30
CO ₃ ⁻²	0.96	4.00
HCO ₃ ⁻	140.00	112.0
Cl ⁻	11.00	19.6
SO ₄ ⁻²	8.00	14.00
Pb	13.42	8.70
Pb ^b	0.96	0.89

^aμg L⁻¹.^bConcentration after decontamination.

has also been studied by using the optimized sorption conditions. The results are reported in Table 5 along with the determined composition of the samples, which shows that an average of 91.3% of lead can be removed from such samples under the existing concentrations of the determined cations and anions. It is, therefore, concluded that easily available sawdust has good potential as a cheap decontaminant for lead from aqueous media.

CONCLUSION

Quantitative adsorption of lead ions from aqueous solutions on sawdust can be achieved within a short contact time of 10 min without any prior chemical treatment or time-consuming adjustments. The reaction was found to be exothermic and occurs in the presence of a variety of anions and cations, with maximum adsorption noted in the presence of 0.005 M HNO₃. The data will be useful in understanding the sorption mechanism of lead on sawdust. This study also concludes that relatively inexpensive sawdust has great potential to be utilized for the removal of lead from aqueous solutions.

REFERENCES

1. Reilly, C. (1980) *Metal Contamination of Food*, 1st ed.; Applied Sci. Publishers: London, Chap. 5, 85–104.
2. Daher, R.T. (1995) Trace metals (Lead and cadmium exposure screening). *Anal. Chem.*, 67 (12): 405R–410R.
3. Cerreia, P.R.M., Oliveira, E., and Oliveira, P.V. (2000) Simultaneous determination of Cd and Pb in foodstuffs by electrothermal atomic absorption spectrometry. *Anal. Chim. Acta*, 405: 205–211.
4. Bankovsky, Y.A., Vircavs, M.V., Veveris, O.E., Peline, A.R., and Vircava, D.K. (1987) Preconcentration of microamounts of elements in natural waters with 8-Mercapto-quinoline and bis(8-Quinolyl) disulphide for their atomic absorption determination. *Talanta*, 34: 179–182.
5. Frigge, C. and Jackwerth, E. (1993) Systematic investigation of multi-element preconcentration from copper alloys by carbamate precipitation before atomic absorption spectrometric analysis. *Anal. Chim. Acta*, 271: 299–304.
6. Li, J., Liu, Y., and Lin, T. (1990) Determination of lead by hydride generation atomic absorption spectrometry. I. A new medium for generating hydride. *Anal. Chim. Acta*, 231: 151–155.
7. Sturgeon, R.E., Willie, S.N., and Berman, S.S. (1989) Atomic absorption determination of lead at picogram per gram levels by ethylation with in situ concentration in a graphite furnace. *Anal. Chem.*, 61: 1867–1869.
8. Khalid, N., Chaudhri, S.A., Saeed, M.M., and Ahmed, J. (1996) Separation and preconcentration of lead and cadmium with 4-(4-chlorophenyl)-2-phenyl-5-thiazo-leacetic acid and its application in soil and seawater. *Sep. Sci., Technol.*, 31 (2): 229–239.
9. Carasek, E., Tonjes, J.W., and Scharf, M. (2002) A new method of microvolume back extraction procedure for enrichment of lead and cadmium and determination by flame atomic absorption spectrometry. *Talanta*, 56: 185–191.
10. Hirata, S., Honda, K., and Kumamru, T. (1989) Trace metal enrichment by automated on-line column preconcentration for flow-injection atomic absorption spectrometry. *Anal. Chim. Acta*, 221: 65–76.
11. Mandaokar, S.S., Dharmadhikari, D.M., and Dara, S.S. (1994) Retrieval of heavy metal ions from solution via ferritization. *Environ. Pollution*, 83: 277–282.
12. Bilinski, H., Kozar, S., Kwokal, Z., and Branica, M. (1977) Model adsorption studies of Pb(II), Cu(II), Zn(II) and Cd(II) on MnO₂ in Adriatic seawater samples. *Thalassia Jugosl.*, 13: 101–108.
13. Muhammad, D. and Hussain, R. (1992) Adsorption of lead from aqueous solutions by poly(methyl Methylacrylate). *Sci. Intern. (Lahore)*, 4 (2): 143–145.
14. Abe, M., Wang, P., Chitrakar, R., and Tsuji, M. (1989) Adsorption and desorption behaviour of heavy metal ions on hydrated titanium dioxide. *Analyst*, 114: 435–438.
15. Vanderborght, B.M. and Grieken, R.E. Van. (1980) Water analysis by spark source mass spectrometry after pre-concentration on activated carbon. *Talanta*, 27: 417–422.
16. Kozar, S., Bilinski, H., Branica, M., and Schwuger, M.J. (1992) Adsorption of Cd(II) and Pb(II) on bentonite under estuarine and seawater conditions. *Sci. Total Environ.*, 121: 203–216.
17. Mareira, J.C., Pavan, L.C., and Gushikem, Y. (1990) Adsorption of Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) from aqueous solutions and 2-Mercaptobenzimidazole-modified silica gel. *Mikrochim. Acta (Wien)*, III: 107–115.

18. Gardner, M.J. and Hunt, D.T.E. (1981) Adsorption of trace metals during filtration of potable water samples with particular reference to the determination of filtrable lead concentration. *Analyst*, 106: 471–474.
19. Kabil, M.A., Abdullah, A.M., Diab, M.A., and Aggour, Y.A. (1985) Extraction of lead ion solutions using polyacrylonitrile and acrylonitrile-charcoal composite. *Fresenius' Z. Anal. Chem.*, 321: 495–496.
20. Bermejo-Barrera, P., Nancy, M.A., Cristina, D.L., and Bermejo-Barrera, A. (2003) Use of amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol as a preconcentration system for river water prior to determination of copper(II), cadmium(II) and lead(II) ions by flame atomic absorption spectroscopy. *Microchim. Acta*, 142: 101–108.
21. Acemiglu, B. and Alma, M.H. (2001) Equilibrium studies on adsorption of Cu(II) from aqueous solution onto cellulose. *J. Colloid Interface Sci.*, 243: 81–84.
22. Khalid, N., Ahmad, S., Kiani, S.N., and Ahmed, J. (1998) Removal of lead from aqueous solutions using rice husk. *Sep. Sci. Technol.*, 33: 2349–2362.
23. Khalid, N., Ahmad, S., Kiani, S.N., and Ahmed, J. (1999) Removal of mercury from aqueous solutions by adsorption to rice husks. *Sep. Sci. Technol.*, 34: 3139–3153.
24. Khalid, N., Ahmad, S., Toheed, A., and Ahmed, J. (2000) Potential of rice husks for antimony removal. *Appl. Radiat. Isot.*, 52: 31–38.
25. Hasany, S.M. and Ahmed, R. (2002) Fixation of micro or submicro amounts of Hg(II) ions onto sawdust from aqueous solutions. *Main Group Metal Chem.*, 25: 719–726.
26. Benes, P. and Majer, V. (1980) *Trace Chemistry of Aqueous Solutions*; Amsterdam: Elsevier, 200–223.
27. Ahmad, S., Khalid, N., and Daud, M. (2003) Cadmium decontamination from aqueous media using lateritic minerals. *Sep. Sci. Technol.*, 38: 2003–2024.