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ADSORPTION STUDIES OF LEAD ON LATERITIC MINERALS FROM AQUEOUS MEDIA

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ABSTRACT

Minerals produced by lateritic weathering have been exploited to evaluate their potential for the decontamination of lead ions from aqueous solutions and for understanding decontamination mechanism in nature. 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 the particular material could be used as an adsorbent. Maximum adsorption was observed at 0.005 mol L^{-1} acid solutions (HNO_3, HCl, and $HClO_4$) using 0.2 g of adsorbent for $4.82 \times 10^{-5}\,\text{mol L}^{-1}$ lead concentration in five minutes 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 range of 2.41×10^{-6}–$9.65 \times 10^{-4}\,\text{mol L}^{-1}$ lead concentration. The characteristic Freundlich constants, i.e., $1/n = 0.42 \pm 0.02$ and $K = 0.57 \pm 0.01\,\text{mmol g}^{-1}$ have been computed for the

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sorption system. The sorption mean free energy from the Dubinin–Radushkevich isotherm is $13.96 \pm 0.74\,\mathrm{kJ\,mol^{-1}}$ indicating an ion-exchange mechanism of chemisorption. The uptake of lead increases with the rise in temperature (278–323K). Thermodynamic quantities, i.e., ΔG, ΔS, and ΔH also have been calculated for the system. The sorption process was found to be endothermic.

Key Words: Adsorption; Lateritic minerals; Lead; Removal

INTRODUCTION

Lead is toxic to human beings and its presence even at trace levels in air, water, and food articles can cause physiological disorders. The harmful effects of lead have been reported extensively in the literature (1–3). The main sources of lead pollution include the use of tetramethyl and tetraethyl lead as gasoline additives, manufacturing of batteries, formation of alloys with antimony, and tin used in power and telephone cables, manufacturing of soldering material, paints, iron and steel, etc. All these sources contribute to making the water toxic beyond $0.05\,\mathrm{mg\ Pb\,L^{-1}}$, the permissible limit for human consumption. Keeping in view the gravity of the situation, particularly toxicity in children, global attention has now diverted towards understanding the behavior of lead in the ecosystem and its metabolism, for adopting measures for its efficient removal from 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. Adsorption of lead on various inorganic materials and organic compounds has been studied by various workers. Among the inorganic sorbents used for lead are oxides of silicon, manganese, aluminum (12,13), activated carbon (14), bentonite (15), hydrated titanium dioxide (16), and modified silica gel (17,18). The organic sorbents for lead include polycarbonate filters (19), polyacrylonitrile and acrylonitrile charcoal composite (20), dithizone-anchored poly(EDGMA–HEMA) microbeads (21). All these methods are effective for the removal of lead from waste or polluted waters but are either time consuming or expensive, hence there is a need to look into other inexpensive and effective methods for this purpose.

The present study deals with a series of experiments to assess the potential of a naturally available lateritic mineral (LM) for the decontamination behavior/mechanism of lead from aqueous solutions. The main constituents of the material are goethite, hematite, magnetite, alumina, and quartz, all of which are good adsorbents (22–24). Moreover, the above-mentioned material is abundantly available at low cost. This is also the continuation of our studies regarding its exploitation for the decontamination of Cr and Ag from industrial effluents (25,26).

EXPERIMENTAL PROCEDURE

Equipment

The absorption measurements were made with a Hitachi model Z-8000 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 $10 \times 0.05\,cm^2$ slot, was used for the air–acetylene flame. A 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 Mathey) 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 1–10, 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 and NaCl and NaOH (pH 8–10). 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 LM used in the present study was obtained from a local deposit. The samples collected from various sites were ground to a particle size of 100 mesh and shaken in a vibrating mill to minimize the associated heterogeneity. This material was then used without any further physical or chemical pretreatment to simulate natural conditions as far as possible.

Sorption Measurements

A known amount of LM 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 ± 1K) 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:

$$\%\ \text{Sorption} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

The distribution coefficient (K_d) was calculated from the equation

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \tag{2}$$

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); and m = amount of adsorbent (g).

Calculation of Thermodynamic Parameters

Thermodynamic parameters were calculated using the following relations:

$$K_c = \frac{C_{ad}}{C_e} \tag{3}$$

where K_c = equilibrium constant; C_{ad} = equilibrium concentration of metal on the adsorbent ($\text{mg}\,\text{L}^{-1}$); and C_e = equilibrium concentration of metal in solution ($\text{mg}\,\text{L}^{-1}$). If F_0 is the fractional attainment of adsorption at equilibrium, then

$$C_e = C_i(1 - F_e) \tag{4}$$

and

$$C_{ad} = C_i F_e \tag{5}$$

where C_i = initial concentration of metal in solution; and F_e = fractional attainment of metal concentration at equilibrium.

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

$$K_c = \frac{F_c}{(1 - F_c)} \tag{6}$$

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:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

where ΔS = entropy change for the process; ΔH = enthalpy change for the process; R = gas constant; and T = absolute temperature.

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

$$\Delta G = -RT \ln K_c \tag{8}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{9}$$

where the symbols have their usual significance.

RESULTS AND DISCUSSION

The adsorption of lead ions from aqueous solutions on LM 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 subsequently 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 ±3.0% unless otherwise specified.

Characterization of Adsorbent

The main mineral constituents of the LM used were determined employing optical microscopy and x-ray diffraction (27). The determined mineralogical constituents have been reported in Table 1, which revealed that the LM is mainly composed of hydrous oxides of iron-bearing minerals. The elemental contents of the LM were characterized by using instrumental neutron activation analysis (INAA) (28,29) and the results are given in Table 2.

Influence of Equilibration Time

The time dependence adsorption of lead on LM was studied using 10.0 cm^3 of 4.82×10^{-5} mol L^{-1} of lead solution in 0.005 mol L^{-1} of HNO_3 with 0.2 g of LM. The equilibration time was varied from 0.5 to 20 min and the results have been shown in Fig. 1. It is seen that the percentage adsorption increases with the increase in equilibration time. Maximum adsorption was observed at 5 min time, beyond which there is no further increase in the adsorption. Therefore, 5 min equilibration time was considered to be sufficient for the adsorption of lead on LM and was employed for all the subsequent experiments. The short

Table 1. Mineral Constituents of the LM

Constituent	Formula
Goethite	$FeOOH$
Hematite	Fe_2O_3
Limonite	$2Fe_2O_3 \cdot 3H_2O$ $FeO(OH) \cdot n\,H_2O$
Magnetite	Fe_3O_4
Quartz	SiO_2
Diaspore	$HAlO_2$
Enstatite	$Mg_2(Si_2O_6)$
Saprolite	
Ilmenite	$FeTiO_3$
Olivine	$MgFeSiO_4$
Dolomite	$Ca{-}MgCO_3$
Bauxite	$Al_2O_3 \cdot 2H_2O$

Table 2. Chemical Composition of LM

Element	%
Fe	34.0–41.0
Mg	3.80–6.33
Al	4.8–9.3
Si	8.63–13.60
Zn	0.01–0.08
Ca	4.23–16.4
Mn	0.51–0.83
Ni	0.31–0.55
Cu	0.07–0.09
Cr	0.35–0.52
Co	0.05–0.08
Ti	0.83–1.89

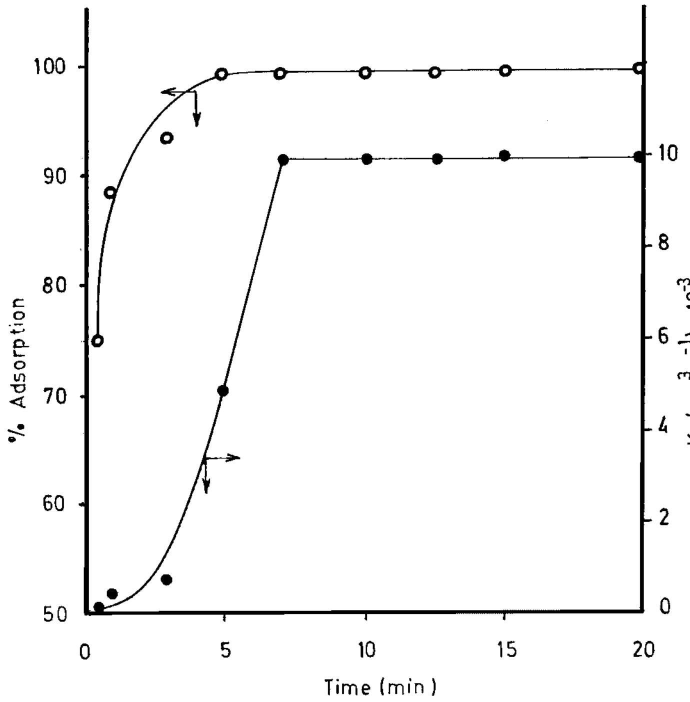
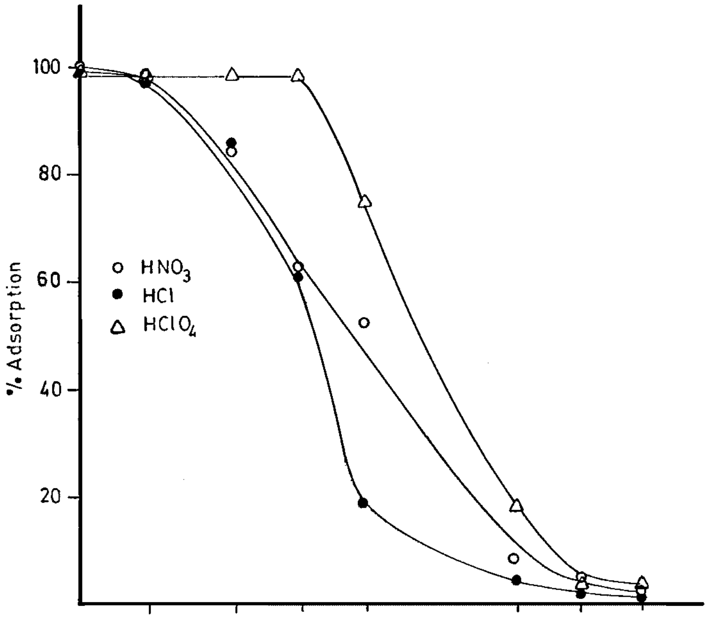


Figure 1. Influence of equilibration time on the adsorption of lead on LM.

equilibration time confirms that the adsorption process is a surface phenomenon proceeding between the hydrolytic products of metal ions and sorbent carrying OH^- groups (30).

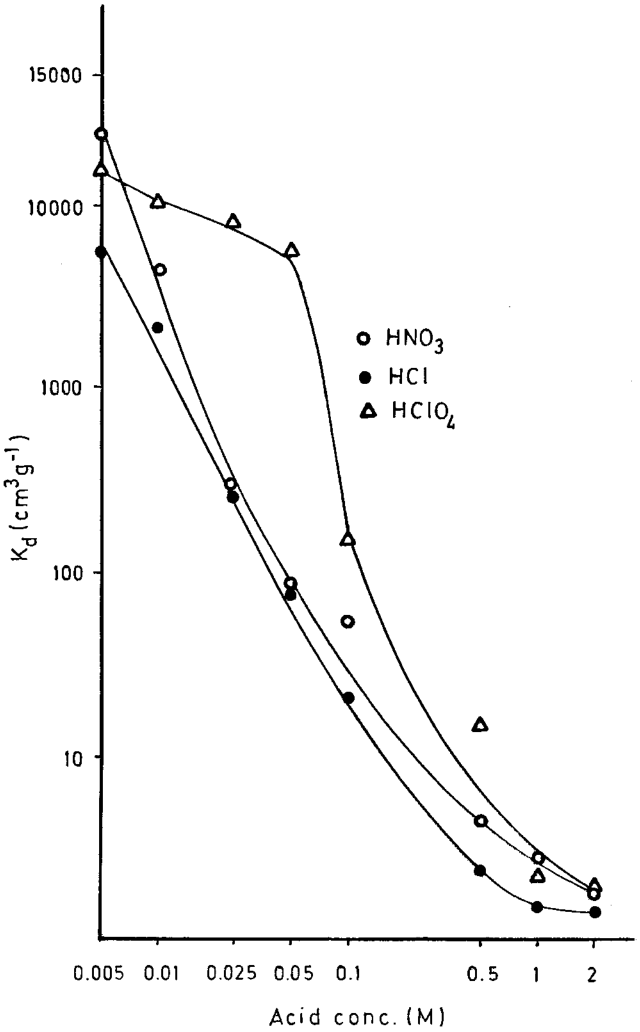
Effect of Acid Concentration

Interaction of various chemical compounds and electrolytes with oxides may alter the surface properties; therefore, the adsorption behavior of lead (4.82×10^{-5} mol 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 LM. Sulfuric acid was not included in this study since it forms insoluble lead sulfate. The lowest concentration of acids used was 0.005 M having a pH of 2.3. Below this acid concentration, the pH of the solution will be higher which is above the



(a)

Figure 2. (a) Variation of percent adsorption of lead on LM as a function of acid concentration. (b) Variation of K_d for the adsorption of lead on LM as a function of acid concentration.



(b)

Figure 2. Continued.

point of zero charge values for quartz and diaspore. Therefore, the presented study was restricted to this concentration only. The results presented in Fig. 2(a) and (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 from 0.005 to 2.0 *M*. Similar trends have been reported for the adsorption of chromium and silver on mineral mixture (25,26). 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. In addition, a higher concentration of acid appears to suppress the 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 LM.

The adsorption of metal ions on hydrous metal oxide surface can probably be explained on the basis of the surface complex formation model. In this model the hydrolysis of silicon dioxide which is the second major constituent of LM, produces hydrous oxide surface group -SiOH, i.e., the silanol group. This results in the formation of silica surface as weakly acidic with $K_a = 10^{-6}\text{–}10^{-8}$ (31). The cation exchange reaction can occur in aqueous solutions as follows:

$$m(\text{–SiOH}) \leftrightarrow m(\text{–SiO}^-) + m\text{H}^+ \tag{10}$$

$$\text{M}^{n+} + m(\text{–SiO}^-) \leftrightarrow \text{M(OSi–)}_m^{n-m} \tag{11}$$

The overall reaction can be represented as:

$$\text{M}^{n+} + m(\text{–SiOH}) \leftrightarrow \text{M(OSi–)}_m^{n-m} + m\text{H} \tag{12}$$

where M^{n+} = metal ion with $n+$ charge; $-SiOH$ = silanol group on SiO_2 surface; and $m\,H^+$ = 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, based on competitive reaction of the protons in the medium, and positively charged lead ions. The maximum adsorption of metal at $0.005\,M$ acid concentration is in accordance with the point of zero charge for SiO_2 and diaspore, which are in the range of 1.8–2.2 (32). This indicates that the adsorption of metal occurs on the surface of SiO_2 present in LM.

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 $4.82 \times 10^{-5}\,mol\,L^{-1}$ of lead solution using the optimized parameters. The amount of LM was varied from 0.05 to 0.6 g and the results have been represented in Fig. 3, which depicts that 0.2 g of LM is

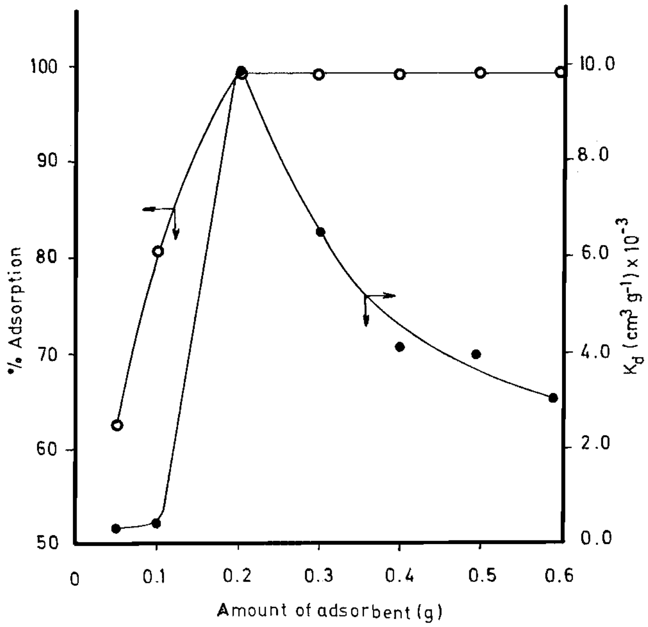


Figure 3. Effect of amount of adsorbent on the adsorption of lead on LM.

sufficient for the quantitative removal of lead from the aqueous solution used and this amount of LM was used for further investigations.

Variation of Adsorbate Concentration

The concentration dependence of lead adsorption on LM 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 L^{-1}. It was observed that the adsorption of lead was almost constant up to 4.82×10^{-5} mol L^{-1} of lead, while beyond this concentration the adsorption decreased. This can be explained in terms of relatively fewer number of active sites at higher concentrations of lead.

The data for the adsorption of lead on LM 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 over the entire range of concentration

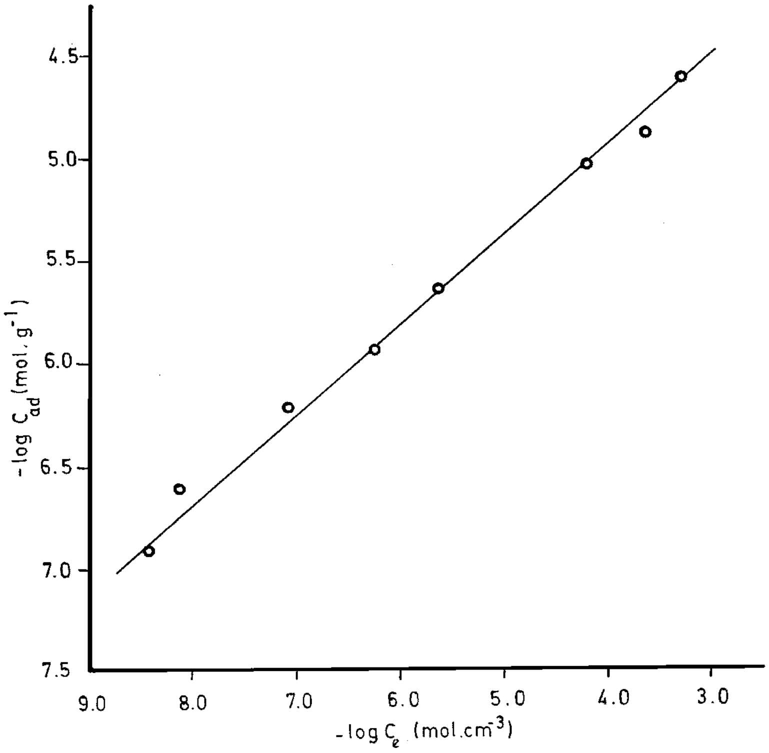


Figure 4. Freundlich adsorption isotherm of lead on LM.

studied. The Freundlich isotherm was tested in the following linearized form:

$$\log C_{\mathrm{ad}} = \log K + \frac{1}{n}\log C_{\mathrm{e}} \tag{13}$$

where C_{ad} = amount of lead adsorbed at equilibrium (mol g^{-1}); C_e = equilibrium concentration of lead in solution (mol L^{-1}); K and $1/n$ = Freundlich constants.

A plot of log C_{ad} vs. $\log C_{\mathrm{e}}$ yields a straight line (Fig. 4). This linear plot supports the applicability of the Freundlich isotherm model in the present study. A similar trend has been reported for the adsorption of silver on mineral mixture (26). The values of Freundlich constants $1/n$ and K give a measure of the adsorption intensity and capacity of the absorbent, respectively. These constants were evaluated from the slope and the intercept of the straight line (Fig. 4) using a least-square fit program and were found to be 0.42 ± 0.02 and 0.57 ± 0.01 mmol g^{-1}, respectively. The fractional value of $1/n$ $(0 < 1/n < 1)$ signifies that the surface of the LM is heterogeneous in nature (33).

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

$$C_{\mathrm{ad}} = C_{\mathrm{m}}\exp(-B\epsilon^2) \tag{14}$$

where C_{ad} is the amount of lead adsorbed on LM, C_{m} is the maximum amount of lead that can be adsorbed on LM under the optimized experimental conditions, B is a constant with a dimension of energy, and Polyanyi potential, $\epsilon = RT\ln(1 + 1/C_{\mathrm{e}})$, where R is the gas constant in kJ mol^{-1} K^{-1}, T is the

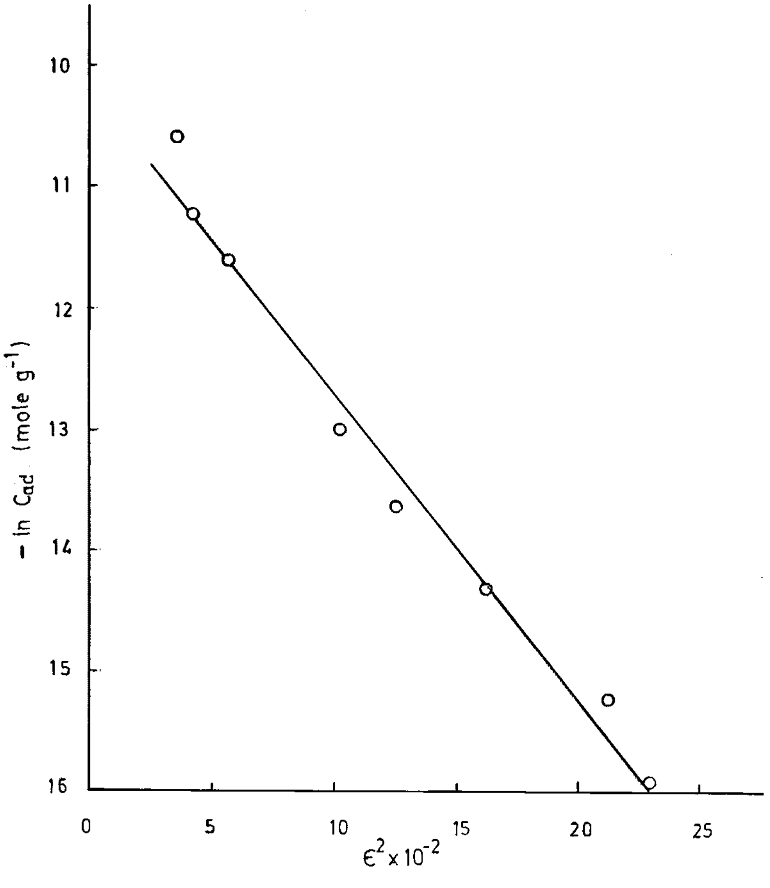


Figure 5. Dubinin–Radushkevich adsorption isotherm of lead on LM.

absolute temperature in K, and C_e is the equilibrium concentration of lead in solution. The obvious linearized form of D–R isotherm is:

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

when $\ln C_{ad}$ is plotted against ϵ^2, a straight line was observed (Fig. 5). The computed values of B and C_m from the slope and intercept of this straight line were $-2.57\times10^{-3} \pm 1.37\times10^{-4}$ kJ mol^{-2} and $4.17\times10^{-5} \pm 7.89\times10^{-7}$ mol g^{-1}, respectively. From the calculated value of B the mean sorption energy (E) was computed as:

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

which is the free energy transfer of one mole of solute from infinity to the surface of LM. The numerical value of E evaluated from Eq. (16) is 13.96 ± 0.74 kJ mol^{-1}, which is in the expected range of 8–16 kJ mol^{-1} for chemisorption or ion exchange (34).

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 affects the adsorption efficiency of an adsorbent. Therefore, using the optimized parameters the adsorption of lead ions (4.82×10^{-5} mol L^{-1}) on LM was also studied in the presence of high concentrations of various cations and anions which are commonly found in samples of ground water. The results are shown in Table 3. All the anions were used as their sodium salts, whereas for cations the

Table 3. Effect of Diverse Ions on the Adsorption of Lead Ions on LM

Ions	Concentration $\times10^3$ (mol L^{-1})	% Adsorption
None	—	99.62
NO_3^-	5.00	99.45
Cl^-	5.00	99.16
ClO_4^-	5.02	97.58
CH_3COO^-	5.08	96.65
Na^+	26.10	95.78
K^+	7.67	96.30
Ca^{2+}	7.48	85.67
Mg^{2+}	12.34	89.96

Table 4. Adsorption Studies of Lead Ions on LM as a Function of Temperature

Temp. (K)	$1/T$ (K^{-1}) ($\times 10^{-3}$)	Concentration Adsorbed ($mol\,L^{-1}$) ($\times 10^{-5}$)	Concentration in Bulk ($mol\,L^{-1}$) ($\times 10^{-7}$)	K_c	$\ln K_c$
278	3.597	4.78	4.34	110.11	4.70
283	3.533	4.78	3.86	124.00	4.82
293	3.413	4.77	4.80	152.85	5.03
303	3.300	4.79	2.89	165.67	5.11
313	3.195	4.80	2.17	221.22	5.40
323	3.096	4.80	1.93	249.00	5.52

LM, 200 mg; shaking time, 5 min; volume equilibrated, 10 cm^3; concentration of HNO_3, 0.005 $mol\,L^{-1}$; concentration of lead, 4.82×10^{-5} $mol\,L^{-1}$.

nitrate salts were used. The perusal of the data in Table 3 shows that the adsorption of lead on LM was quantitative in the presence of all the ions studied except calcium and magnesium, which decreased the adsorption by 14 and 10%,

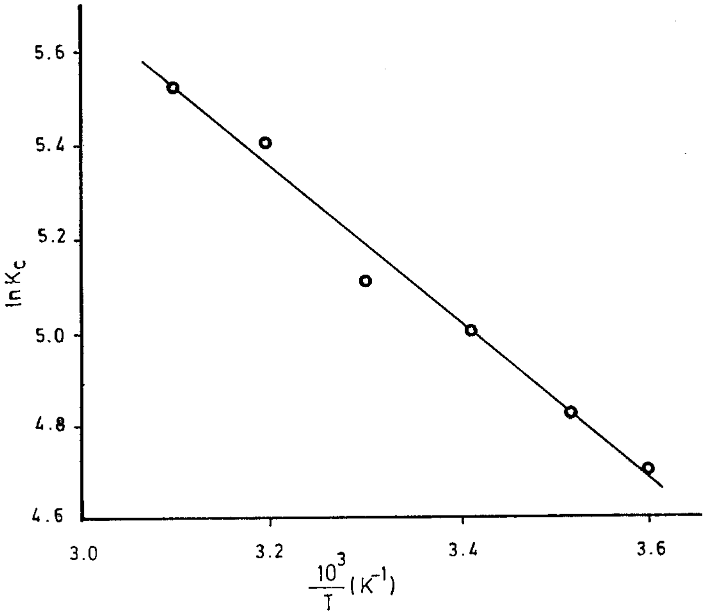


Figure 6. van't Hoff plot for the adsorption of lead on LM.

Table 5. Thermodynamic Parameters for Adsorption of Lead Ions on LM

Temperature (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
278	−10.87	13.48	87.57
283	−11.34	13.48	87.70
293	−12.25	13.48	87.81
303	−12.87	13.48	86.97
313	−14.05	13.48	87.95
323	−14.82	13.48	87.60

respectively. This decrease in the adsorption of lead is probably due to the utilization of the adsorption sites on the surface of LM by these ions.

Effect of Temperature

The effect of temperature on the adsorption of lead ions (4.82×10^{-5} mol L^{-1}) on LM was also checked using the optimized conditions. The temperature was varied from 278 to 323K. The amounts of lead ion adsorbed at various temperatures are shown in Table 4, which reveals that the uptake of lead increases with the rise in temperature, indicating better adsorption at higher temperature. Similar results have also been reported for the adsorption of silver on mineral mixture (26). The increase in the amount of lead adsorbed at equilibrium with an increase in temperature may be either due to acceleration of some originally slow adsorption steps or due to the creation of some new active sites on the adsorbent surface.

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_e vs. $1/T$ was a straight line (Fig. 6). The slope and intercept of this line were equal to ($-\Delta H/R$) and ($\Delta S/R$), respectively, thus allowing us to calculate ΔH and ΔS. By using the Eq. (7) the estimated ΔH value for the present system was 13.48 kJ mol^{-1} (Table 5). 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 5. The negative values of ΔG indicate that the adsorption of lead on LM occurs via spontaneous process. The increase in the numerical value of $-\Delta G$ with the rise in temperature indicates that the sorption process of lead ions on LM becomes more favorable at higher temperatures. The positive value of enthalpy change (ΔH) confirms the endothermic adsorption of lead on LM. The positive value of ΔS suggests the increased randomness at the solid–solution interface during the adsorption of lead on LM.

CONCLUSION

Quantitative adsorption of lead ions from aqueous solutions on LM can be achieved within a short contact time of five minutes without any prior chemical treatment or time consuming adjustments. The reaction was found to be endothermic and occurs in the presence of a variety of anions, with maximum adsorption noted in the presence of 0.005 *M* HNO_3. This data will be useful in understanding the sorption mechanism and pathway of lead in lateritic soil during the migration in ecosystem. On the basis of this study, it is concluded that abundantly available inexpensive LM, which finds little utility in general, has great potential to be utilized for the removal of lead from aqueous solutions by making sieves or granules. The loaded material can be converted into bricks for its safe disposal.

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