ADSORPTION BEHAVIOR OF LEAD IONS ON PYROPHYLLITE SURFACE

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Abstract: The alumino-silicate based adsorbent pyrophyllite mineral was studied for its possible application as an adsorbent for the removal of aqueous lead using the adsorption technique. The effects of different types of pyrophyllite, initial concentration of thelead ion, contact time, temperature and solution pH on the adsorption of lead ions were studied by equilibrating, batchwise, different amounts of pyrophyllite with aqueous solutions of different concentrations. It has been found that pyrophyllite is effective in removing 74 to 99% of lead ions from aqueous solutions. The initial rate of adsorption of lead increases with time up to 30 min and thereafter it reaches equilibrium. The rate of adsorption was inversely affected by an increase in initial concentration of lead. The Langmuir adsorption isotherms were used to represent experimental data. The adsorption process follows first order kinetics and is found to be endothermic.

Introduction

Lead is one of the highly toxic metal ions widely dispersed in the earth's crust and soils. It generally contains 2 - 200 μg of lead per gm of soil[1,2]. Galena is the chief source of the extraction of lead. By weathering, the insoluble PbS present in the lean `refuse-heap' is converted to soluble lead ions and may lead to contamination of water bodies. The main industrial sources of water soluble lead ions include storage battery and television tube manufacturing, sulphuric acid, production by lead chamber process, printing and paints industries and ceramic glazes. The wide industrial applications and mining/extraction activities are the main sources for the presence of heavy metal ions in soil, water and in the environment.

The methods available for the removal of heavy metal ions, including lead from industrial effluents are: (i) chemical precipitation in the form of insoluble species, (ii) ion exchange, (iii) foam flotation (iv) reverse osmosis (v) solvent extraction and (vi) adsorption. The chemical precipitation method leads to the generation of solid or wet sludge posing disposal problem. The methods (ii) to (v) are not very cost effective, especially for the treatment of high volume/high concentration effluents. Sorption at solid substrate materials is considered as the most suitable process for the removal of heavy metal ions from solutions at low concentrations. In recent years, clays and related minerals have been explored as sorbents for heavy metals. However, their industrial and environmental applications as sorbents are extremely limited. Till date, the only sorbent typically used for low concentration of heavy metal ions is active carbon, which adsorbs relatively low amounts of metal ions and is very unselective to the type of metal under consideration. The activated carbon has been shown to adsorb 94% lead from a solution containing 10 ppm lead ions. The severe limitation of sorption process using activated carbon, however, lies in the high cost of the substrate material and the significant cost[2] involved in its periodic regeneration.

If a cheaper and recyclable adsorbent can be found, the treatment of heavy metal ions present in aqueous solutions/effluents could be possible. In pursuance of this objective, the present paper describes the studies carried out on the sorption of lead ions from aqueous solutions on pyrophyllite, an abundantly available, rather inexpensive, hydroxy-aluminosilicate mineral.

Experimental Studies

Materials/Equipments

Representative samples of normal pyrophyllite (NP) and sericitic pyrophyllite (SP) were procured from M/S Eastern Mineral, Jhansi (U.P.), India. The particle size of the powder samples were from range 45 - 75 microns. The samples (1 kg) were sized and ground separately for experimental work. The representative ground samples, taken after coning and quartering, were subjected to wet chemical analysis (Table-1). Dionex 500 Ion Chromatography/GBC-902 Atomic Absorption Spectrophotometry was used for the analysis of Pb^{++} ions. A Phillips X-ray diffractometer (Model 1710) was used with nickel filtered Cu-K_α radiation to identify the mineralogical composition of the pyrophyllite samples used in the present studies which confirmed the samples to be 2-layer, monoclinic type. An electric rotary shaking machine and a Systronic digital pH meter were used for equilibration and pH measurement of the solution.

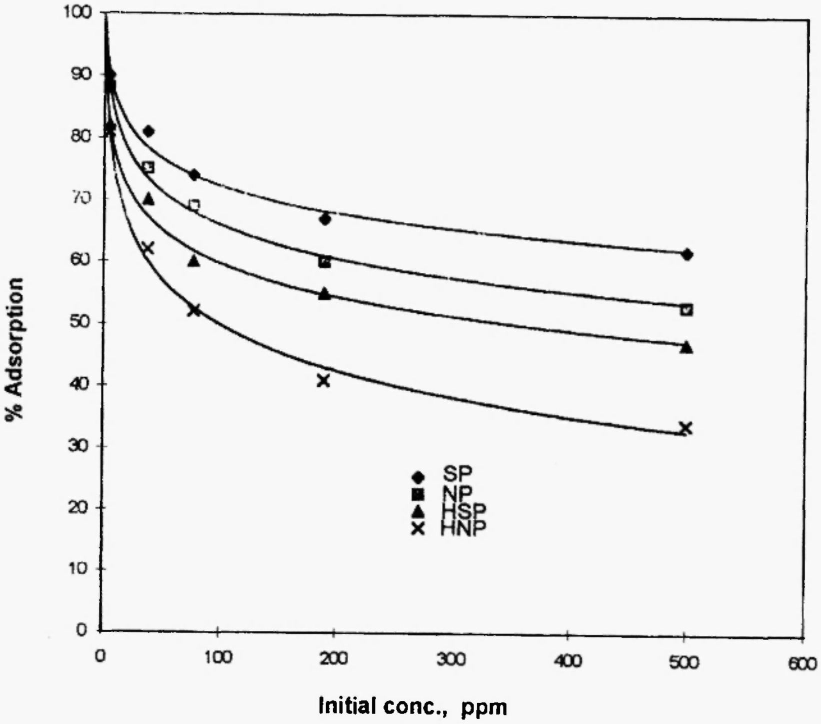

Fig. 1: Effectiveness of different types of Pyrophyllites on adsorption.

***Experimental methods* (Batch studies)**

The adsorbent, pyrophyllite sample is a microcrystalline and porous mineral having a large surface area (approx. 0.145 m^2/g) and wide particle size distribution. The adsorbent was graded in different sizes and after lead removal studies with these fractions, <75 micron size was chosen for the overall study.

Batch adsorption studies were carried out at room temperature with accurately weighed pyrophyllite powder added to 100 ml test solutions of lead of specific concentration (5.0, 10.0, 35.0, 50.0, 100.0 and 500.0 mg/l) and the equilibrating mixtures were placed in a stoppered glass bottle and agitated in a temperature controlled shaker for 30 minutes using a mechanical shaker. Thereafter, the solution was allowed to stand for 25 minutes and then filtered through a No. 42 Whatman filter paper. The pyrophyllite powder, retained on the filter paper was thoroughly washed witn distilled water to collect the soluble lead ions (non adsorbed) in the filtrate and the volume of the filtrate was made up to 200 ml. After appropriate dilution, to bring the concentration of lead ions in the range of the instrument, the lead concentration was analysed.

Reagents: All the chemicals used were of analytical grade. A stock lead solution (1000 mg/l) was prepared from lead nitrate using double distilled water and was used to prepare test solutions.

Results and discussion

The effects of different types of pyrophyllite samples, concentration of adsorbate and pH on the adsorption characteristics of lead ions from aqueous solutions were investigated. The results obtained are discussed below.

Table 1: Chemical analysis of the sericitic pyrophyllite (SP) sample.

Constituents	Weight percent
SiO_2	53.00
Al_2O_3	28.14
Fe_2O_3	0.61
TiO_2	0.10
MgO	1.09
CaO	1.63
K_2O	9.21
Na_2O	0.32
Loss on Ignition L.O.I.	5.55

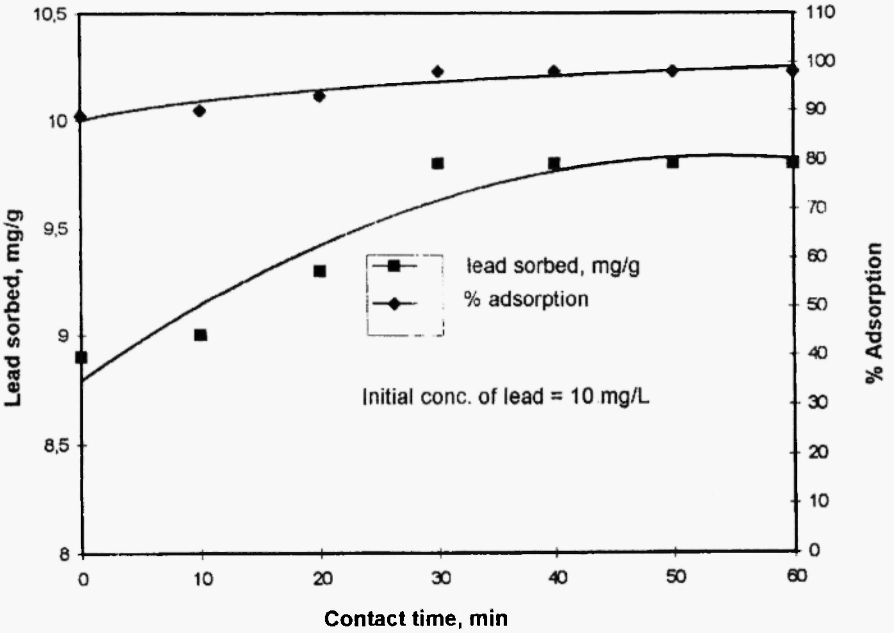

Fig. 2(a) : Plot of contact time vs amount of lead sorbed and %

(i) *Effectiveness of different types of pyrophyllite.*

The plot of percentage adsorption versus initial lead ion concentration in test solutions on normal pyrophyllite (NP), sericitic pyrophyllite (SP), heat treated normal pyrophyllite (HNP) and heat treated sericitic pyrophyllite (HSP) is shown in Fig. 1. The heat treatment of the pyrophyllite samples was carried out in air at 1100°C for 2 hours. The percentage adsorption of lead ions is observed to follow the order SP > NP > HNP > HSP. For all the four types of pyrophyllite samples, the percentage adsorption decreases with increasing initial lead ion concentration in solution.

Pyrophyllite is a three-layered mineral in which adioctahedral layer of O-Al-OH is sandwiched between two tetrahedral Si_4O_{10} sheets. As suggested by Andreet et al.[8], who studied the adsorption of nickel ions on pyrophyllite mineral, the adsorbing lead ions are chemisorbed through interaction with oxygen atoms of Al-OH at edge sites. In the case of sericitic pyrophyllite (SP), some of the Si atoms are replaced by aluminium, sodium/potassium ions (to balance charges). Some of the alkali metal ions in pyrophyllite are cation exchangeable and hence during adsorption, lead ions substitute them in addition to chemisorption at Al-OH present at the edge sites. This idea gains support from the fact that cation exchange capacity (C.E.C.) of SP (0.6615meq/g) is higher than that of NP (0.199meq/g). Further it is experimentally observed that SP contain 9.53%, whereas the NP contains only 1.17 % alkali metal ions.

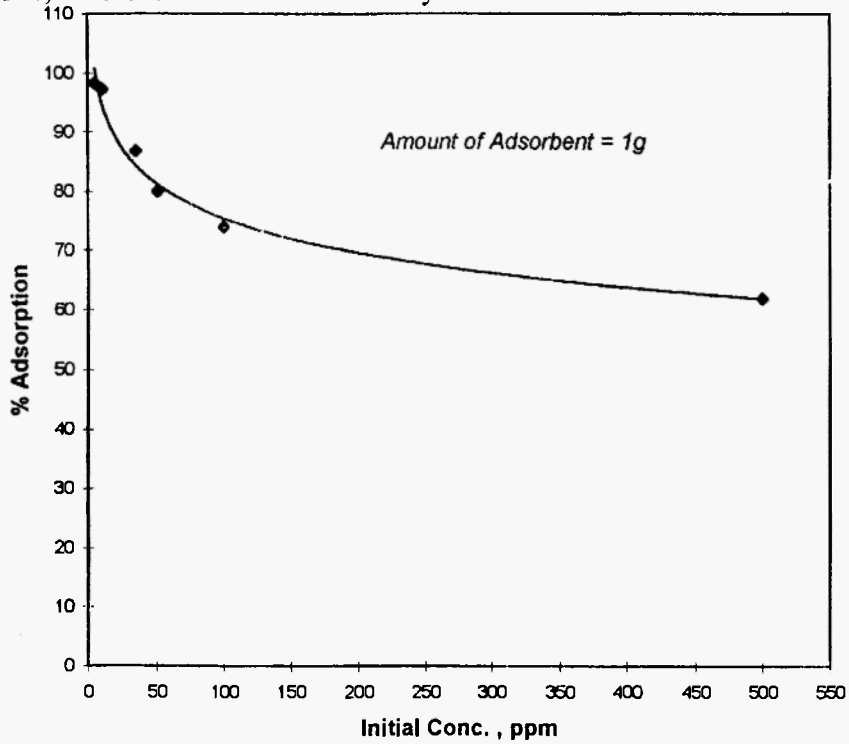

Fig. 2(b) : Effect of Initial concentration vs % Adsorption.

The heat treatment of pyrophyllite affects its structure. On heating, the structural water molecules are gradually removed by breaking of Al-OH bonds present in the Al-OH octahedral layer, in the temperature range 550 to 900^{0}C forming dehydroxylate pyrophyllite. This phase is stable upto 1100^{0}C, after which the formation of mullite starts. The reduction in adsorption sites on heat treatment of pyrophyllite is responsible for the observed decrease in the percentage removal of lead ions as compared to their respective non heat-treated samples.

As observed from above results, the percentage adsorption of lead ions is highest for sericitic pyrophyllite (SP) and hence further studies were carried out on this type of pyrophyllite sample only.

Table 2: Effect of Concentration on Sorption of Pb^{2+} at room temperature (25^{0}C).

Pb^{2+} concentration, mg/l Initial,	Final	Pb^{+2} sorbed, mg/g	Pb^{+2} sorbed, %	Rate constant, k x10^3, min^{-1}
5.0	0.05	0.495	99.00	151.9
10.0	0.20	0.980	98.00	129.0
35.0	4.90	3.010	86.00	64.8
50.0	10.00	4.000	80.00	54.8
100.0	26.00	7.400	74.00	53.1
500.0	175.00	32.50	65.00	34.6

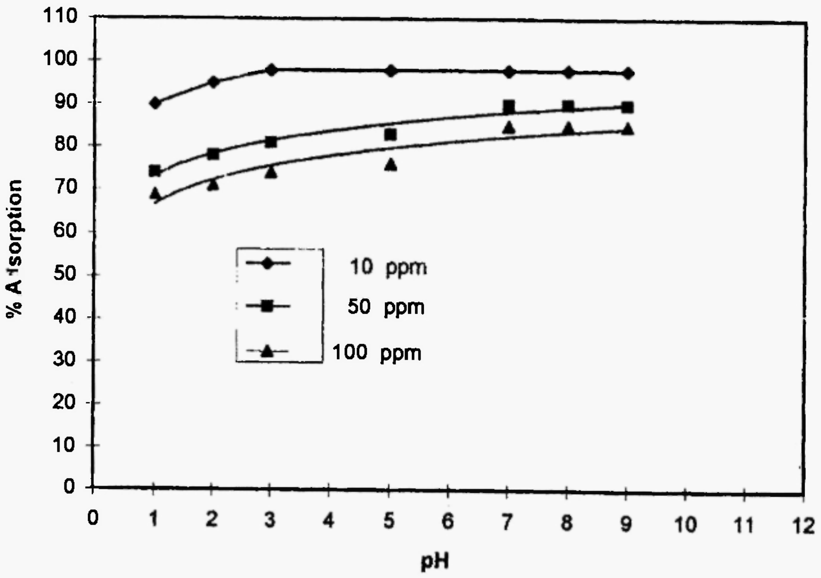

Fig. 3 : Effect of pH on percent Adsorption.

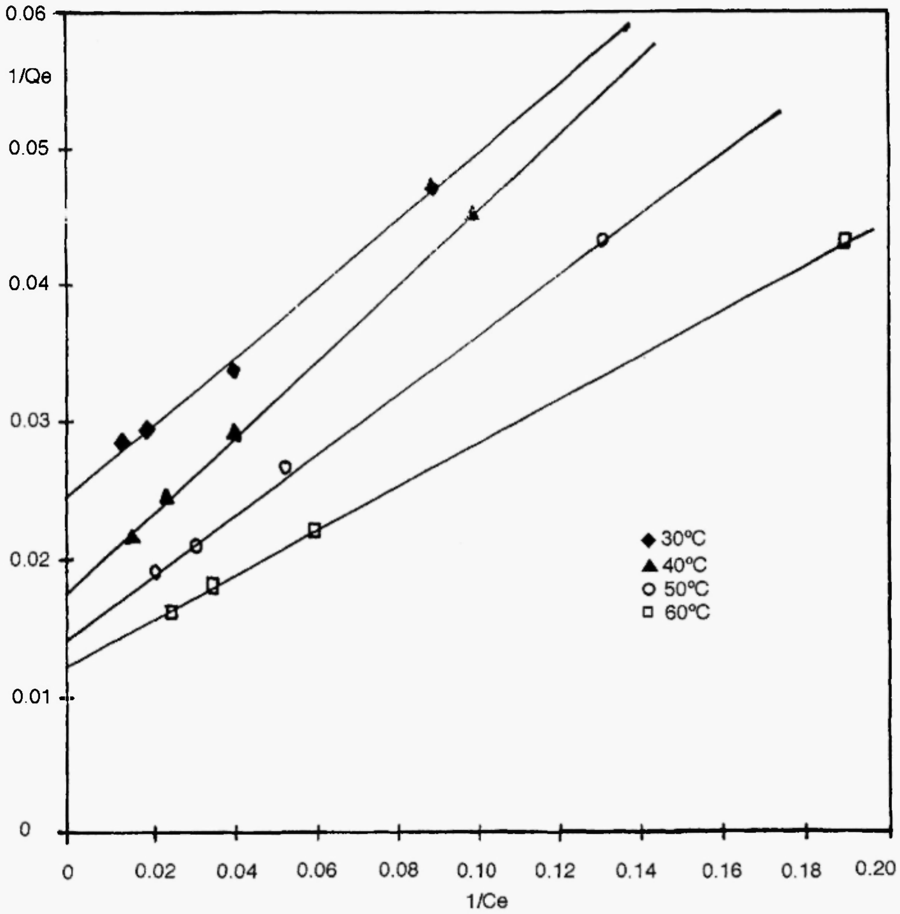

Fig. 4 (a) : Langmuir Isotherm plot for the removal of lead ions by pyrophyllite at different temperatures.

(ii) ***Effect of contact time and of initial concentration.***
The effect of contact time on percent adsorption from aqueous solution of 10 ppm lead ions on 0.5 g powdered SP sample is shown in Fig. 2. It is observed that initially, upto 30 min of contact time, the % adsorption increases; whereafter it becomes constant. This shows that equilibrium is attained in 30 min and hence further experiments were done by fixing contact time of 30 min.

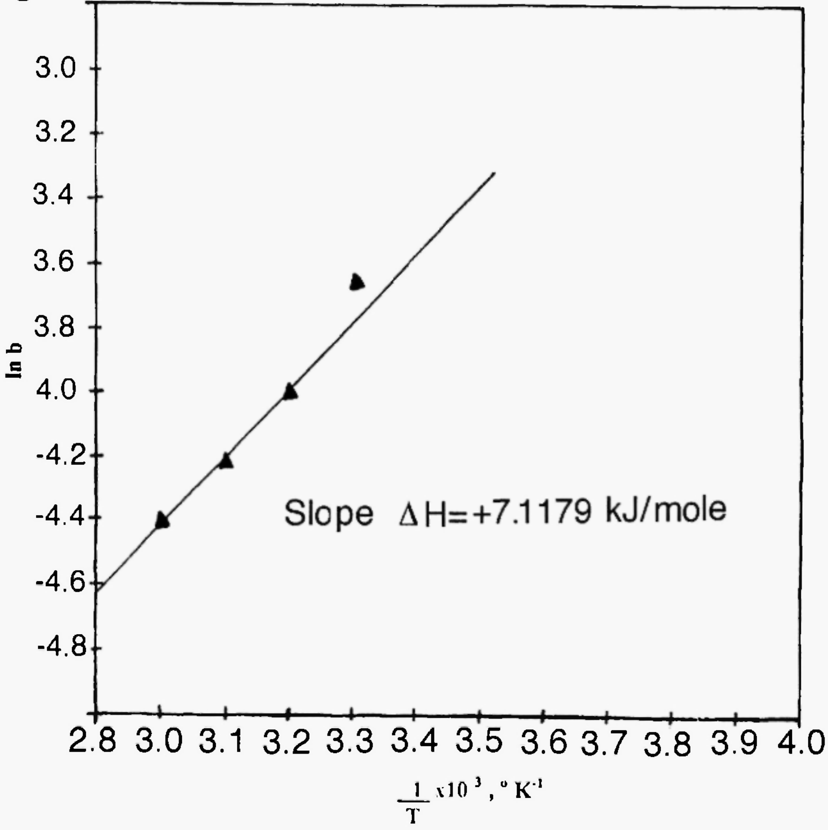

Fig. 4 (b) : Plot of ln b vs 1/T for lead.

The plot of % adsorption of lead ions on a fixed quantity (0.5 g) SP powder versus initial (bulk) concentration of lead ions, in the range 5 to 500 ppm, shows that the % adsorption decreases with increasing concentration (cf. Fig. 3.), similar to the observation made by Shubha and Anirudhan [10]. It is probable that the % adsorption is governed by the ratio (N/S) of initial number of moles (N) of metal ions to the available adsorption active sites (S). This appears to be the reason for better removal (~99.0%) of lead ions when initial concentration was low i.e., 5.0 ppm. The quantity of lead ions adsorbed is, however, found to increase with increase in initial concentration of lead ions. For example, the quantity of adsorbed lead ions is found to be 3.01, 4.0 and 32.5 mg respectively from lead ion solutions containing 35.0, 50.0 and 500.0 ppm initially. The rate constant of the adsorption process for different initial concentration of lead ions in solution were calculated for different temperatures. The rate constants at any given temperature are observed to decrease with increase in the initial concentration. The plot of rate constant versus In C_O /C_e at 25° C (cf. Fig. 4) is observed to be a straight line, confirming the adsorption process to be of first order.

(iii) ***Effect of solution pH.***
The effect of the solution pH on the percentage adsorption from aqueous solutions containing 10, 50 and 100 ppm of Pb^{+2} in contact with 1.0 g of SP for 30 min. was

studied in the pH range 1.0 to11.0. The results are given in Fig.5. It is observed that as the solution pH is made increasingly acidic below pH = 3.0, the % adsorption decreases markedly for all the concentrations of lead ions. However, with an increase in pH up to 11.0, there is only a marginal increase in % adsorption of lead ions. As discussed earlier in this paper, the adsorption of lead ions on SP surface occurs by chemisorption as well as cation exchange mechanisms. However, in highly acidic solutions (pH < 3.0), the exchangeable alkali metal ions may be neutralised leading to a decrease in the % adsorption of lead ions.

(iv) ***Adsorption Isotherms:*** In order to determine the adsorption capacity of the SP pyrophyllite the sorption data were analysed by a computer simulation technique to fit Langmuir isotherms.

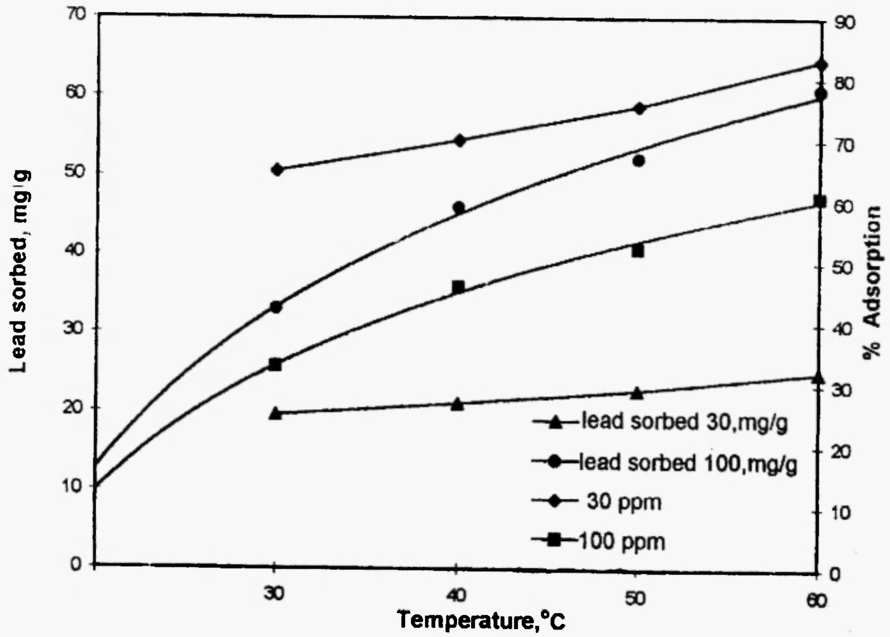

Fig. 5 : Effect of temperature vs lead sorbed and % Adsorption.

The coefficients of this model were computed using linear least squares fitting. The thermodynamic parameters ΔG, ΔS and ΔH were computed from the following equations:

$$\ln(1/b) = -\Delta G/RT \qquad \text{..........} \quad \text{(i)}$$

$$\Delta S = \Delta H - \Delta G/T \qquad \text{..........} \quad \text{(ii)}$$

LANGMUIR ISOTHERM: the Langmuir adsorption isotherm was used to investigate the sorption process. It can be expressed as,

$$\frac{1}{q_e} = \frac{1}{\theta^o b} \cdot \frac{1}{C_e} + \frac{1}{\theta^o} \qquad \text{............} \quad \text{(iii)}$$

where q_e = amount of Pb^{2+} sorbed per unit weight of adsorbent (mg/g)
C_e = equilibrium concentration of in aqueous solution (mg/L)
θ^o and b = Langmuir constants related to the capacity and energy / intensity of adsorption respectively (mg/g and L/mg)

Table 3: Langmuir Constants and Thermodynamic Parameters at different temperatures.

Temperature, K	Langmuir constants θ^0 (mg/g)	$b \times 10^{-3}$ (L/mg)	Thermodynamic properties $-\Delta G$ (kJ /mole)	ΔS (J /mole)	ΔH (kJ /mole)
303	43.47	75.8	6.502	26.9×10^{-3}	1.672
313	56.8	65.5	7.097	28.0×10^{-3}	
323	68.9	63.6	7.400	28.1×10^{-3}	
333	90.9	64.2	7.600	27.8×10^{-3}	

The applicability of the above model for the present system, showing the formation of the monolayer coverage of the adsorbent has been justified by the observation of a linear plot of $1/q_e$ vs $1/C_e$ (cf. Fig. 6). The values of θ^0 and b at different temperatures were determined from the slope and intercept of the linear plot and are shown in Table-3. The Langmuir constant, θ^0, which is related to sorption capacity is observed to increase at higher temperatures. For testing the fitting of the data to the Langmuir isotherm, a dimensionless equilibrium parameter, which is also known as correlation coefficient (R) was calculated using the following equation at different temperatures and initial concentrations. `R' is the essential characteristic of Langmuir isotherm and the main criteria for testing the data. The values of R, lying between zero and one (Table-4) indicate the favourable sorption of Pb^{-+} on pyrophyllite.

$$R = \frac{1}{1 + b C_0} \qquad \text{.............} \quad \text{(iv)}$$

Table 4: Sorption Rate Constants (K), Equilibrium Sorption Capacities (q_e) and Equilibrium Parameter (R) at Different Temperatures and Initial Concentrations.

Init. Conc.	Temperature											
	30^{0}C			40^{0}C			50^{0}C			60^{0}C		
mg /L	$K \times 10^3$ (min^{-1})	q_e (mg/g)	R	$K \times 10^3$ (min^{-1})	q_e (mg/g)	R	$K \times 10^3$ (min^{-1})	q_e (mg/g)	R	$K \times 10^3$ (min^{-1})	q_e (mg/g)	R
30	34.6	19.5	0.30	39.7	21.0	0.33	46.6	22.7	0.34	58.4	24.9	0.34
50	25.7	27.1	0.20	27.0	28.0	0.23	31.9	31.0	0.24	36.3	33.4	0.24
80	16.8	32.0	0.14	25.6	43.2	0.16	29.6	47.4	0.16	34.6	52.0	0.16
100	13.2	33.0	0.11	20.3	46.0	0.13	24.3	52.2	0.14	30.9	60.8	0.13

(v) *Effect of Temperature*. The uptake of Pb^{2+} increases from 19.5 mg/g (65.0%) to 24.9 mg/g (83.0%) for 30 ppm Pb^{+2} solution by increasing temperature from 30^{0}C to 60^{0}C as shown in Fig. 7. The significant increase in sorption capacity of pyrophyllite with the gradual increase in temperature indicates the sorption process to be endothermic as generally observed[11,12,13] because an increase in temperature favours the adsorption process through activating the adsorption sites.

The thermodynamic parameters ΔG, ΔS and ΔH were computed for different working temperatures and are shown in Table-3. The values of the thermodynamic parameters indicate and support that the over all process of adsorption is spontaneous and endothermic. The negative values of ΔG indicate the process to be feasible while the positive values of enthalpy change (ΔH) of sorption, as calculated from the slope of ln b vs 1/T plot (Fig. 8), confirm the process to be endothermic. The positive values of ΔS suggest the increased randomness at the solid-solution interface during sorption[14]

Conclusions

The following conclusions can be drawn from the above studies.

1. Among the four different types of pyrophyllite samples, the sericitic pyrophyllite is found to be the most effective in adsorption (removal) of lead from aqueous solutions.
2. 99 - 74% lead removal is possible from synthetic aqueous solutions containing 5 to 50 mg/l Pb^{2+} ions respectively.
3. An alkaline pH of solutions is more favourable for removal of lead ions as compared to the acidic pH.
4. The adsorption of lead ions on sericitic pyrophyllite is found to follow first order reaction kinetics and to be endothermic.

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References

1. Ying Ma. Qi., Logan T.J. and Traina S.J., *Environ. Sci. Technol.* 1995, **29**, 1118.
2. R. L. Stubs, In '*Lead in the environment*': Applied Science Publishers Ltd: Zoological Society of London, Regent's Park, London, 1973; pp 1-7.
3. E. L.Thackston, D. J. Wilson, J. S. Hanson, D. L. Miller, Jr. *J. Water Pollut. Control Fed.*, 1980, **52**, 317.
4. C. P. Huang and O. Hao,.J *Environ. Technol. Letr.*, 1989, **10**, 863
5. L. Daze, S. Mendioroz and J. A. Pajares., *Clays and Clay Minerals*, 1991, **39**, 14.
6. J. M. Zamzow, B. R. Eichbaum, K. R. Sandgren and D. R. Shanks, *Sep. Sci. Technol.*, 1990, **25**, 1555.
7. H. Koshima., H. Onishi, *Talanta.* 1986, **33**, 391.
8. A M.,Scheidegger A. M. Lamble G. M., Sparks D.L., *Environ. Sci.Technol.* 1996, **30**, 548.
9. S. S. Amritphale, N. Chandra and R. Kumar, *J. Mater. Sci.*, 1992, **27**,4797.
10. K. P. Shubha and T. S. Anirudhan, *Ind. J. Chem. Technol.* 1996, **3**, 55.
11. C. Raji , T. S. Anirudhan, *Ind. J. Chem. Technol.*, 1996, **3**, 345.
12. D. K. Singh, D. P. Tiwari and D. N. Saksena *Indian J. Environ.Hlth.*, 1993, **35**, 169.
13. D. S. Ranjana and N. S. Rawat, *Indian J. Environ. Hlth.* 1993, **35**, 262.
14. C. Raji and T. S. Anirudhan, *Indian J. Chem. Technol.*, 1996, **3**, 49.

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