

APPLICATIONS OF SERICITE IN WASTEWATER TREATMENT : REMOVAL OF Cu(II) AND Pb(II) FROM AQUEOUS SOLUTIONS

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Abstract : The aim of this study is to assess the applicability of sericite in wastewater treatment particularly the removal of two important heavy metal toxic ions viz., Cu(II) and Pb(II) from aqueous solutions. The batch type experiments showed that sericite is found to be one of useful natural sorbent for the removal of these two cations from aqueous solutions and it is also to be observed that with the increase in sorptive concentration amount of metal uptake increases and the concentration dependence data obtained are fitted well for the Langmuir adsorption isotherm rather than Freundlich adsorption model. Further, the Langmuir monolayer adsorption capacity is found to be 1.674 mg g⁻¹ for Cu(II) and 4.697 mg g⁻¹ for Pb(II). Kinetic studies enabled, an apparent equilibria can be achieved between solid/solution interface within ca 10 mins for Cu(II) and ca 90 mins for Pb(II). Moreover, the removal behavior of sericite for these two metal ions is greatly influenced by solution pH.

Key Words : Sericite, Wastewater Treatment, Cu(II), Pb(II), Adsorption

INTRODUCTION

The removal of heavy metal toxic ions from wastewaters has received an increased attention in recent decade for global awareness of the underlying detriment of heavy metals in the environment. Applications of traditional treatment techniques need enormous cost and continuous input of chemicals, which become impracticable and unconventional and also caused for further environmental damage. Moreover, beyond the certain limit the conventional methods viz., chemical precipitation, electrode-deposition, membrane separations, evaporation, solvent extraction etc., are technologically inapplicable. Hence, the interest lies for more effective, economic and

eco-friendly techniques is to be developed for fine-tuning of effluent wastewater treatment.^{1,2)}

In this regard ion-exchangers play a prominent role for the removal/speciation of several cationic/anionic species in waste waters and if the adsorbent is chosen so carefully and the solution chemistry adjusted accordingly, it can provide an effective waste treatment even at wide range of solution pH.³⁻⁶⁾ Interestingly, the adsorption process may also offer to remove effectively/efficiently inorganic- and organic-complexed metals that would not be removed by conventional treatment methodologies.⁷⁻⁹⁾

Applications of clay and minerals in waste water treatment, particularly the speciation/removal of heavy metals, has long been assessed because of their high specific surface area, chemical & mechanical stability, variety of structural and surface properties, higher values of cation exchange capacities etc.¹⁰⁻¹⁸⁾ Presence

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of both Bronsted and Lewis acidity on clay surface further enhances its adsorption capacity.¹⁹⁾ Moreover, since the clays are able to exchange their alkali metal cations with protons, hence they can behave as a buffering medium in controlling the pH of lakes undergoing acid rain.²⁰⁾ Sericite is a layered silicates mineral, generally recognized as white fine powders of muscovite in form, with nano-sized layer structure, interlayer spacing of (002) plane is 10 Å. It has been reported that it is widely used in the alkali flux²¹⁾ and cosmetics²²⁾ however; the application in wastewater treatment is yet to be explored. Hence, in a quest for eco-friendly and cost effective cleaner technologies we attempted to exploit the abundantly available sericite for the removal of two important heavy metal toxic ions viz., Cu(II) and Pb(II) from aqueous solutions.

MATERIALS AND METHODS

Materials

Sericite was obtained from the Keumnam deposit, Gagok-myun, Samcheok City, Kangwon province, Korea. Sample was crushed and sieved to obtain 14~16 mesh size by using mechanical sieve. No further treatment was made before applying it as an adsorbent for present investigation. Sericite sample contains various metal oxides; quantitatively it was analyzed and given in Table 1.

Table 1. Percentage composition of various metal oxides in sericite

Metal Oxides	Composition(%)
SiO ₂	70.12
Al ₂ O ₃	17.97
Fe ₂ O ₃	0.71
CaO	0.27
MgO	1.36
K ₂ O	6.07
Na ₂ O	0.14

Copper (CuSO₄ • 5H₂O; GR Reagent, Duksan Pure Chem., Co. Ltd., Korea) and lead (Pb(NO₃)₂;

GR Reagent, Shinyo Pure Chem. Co. Ltd., Japan) salts were used of GR grade. The stock solutions (0.1 mol L⁻¹) of the Cu(II) and Pb(II) were prepared by dissolving the exact quantity of respective salts in double distilled water. The stock solution was further diluted to the required experimental concentration. The other chemicals used were of AR or equivalent grades.

Methodology

Batch experiments were performed to obtain the adsorption data with the variation of time, sorptive concentration, pH and ionic strength. The adsorption of Cu(II) or Pb(II) was investigated by taking 0.20 g of sericite (14~16 mesh size) in 0.10 L of sorptive solution at the desired concentration. Equilibrated the solution mixture for the desired length of time in an automatic shaker at constant temperature i.e., 25±2 °C. After equilibration the sample was taken out and was filtered with 0.2 µm syringe filters, and the bulk metal concentration was measured by using Atomic Absorption Spectroscopy (Varian Spectra AA-300). While doing the pH dependence study the pH adjustment was made by addition of drops of strong HNO₃/NaOH.

RESULTS AND DISCUSSION

Speciation of Cu(II) and Pb(II)

To evaluate Cu(II) & Pb(III) removal through the adsorption process without precipitation, speciation of Cu(II) and Pb(II) was simulated with MINEQL, a geochemical simulation program, to find out what concentration of Cu(II) & Pb(II) and pH can be applicable without their precipitation. Hence, various species of Cu(II) and Pb(II) in solutions were analyzed at initial sorptive concentration of 3.15 x 10⁻⁴ mol L⁻¹ (for Cu(II)) and 1.93x10⁻⁴ mol L⁻¹ for Pb(II) at constant ionic strength 0.001 mol L⁻¹ NaNO₃ and at constant temperature 25 °C using this MINEQL simulation program. The simulation results obtained are shown in Figures 1&2,

which clearly indicate that at these concentrations up to pH~5.8 both copper and lead exists in its ionic form i.e., Cu^{2+} and Pb^{2+} and beyond that they form the tenorite or precipitated. Hence, keeping it in view almost similar concentration for Cu(II) and much lower concentration i.e., $9.65 \times 10^{-5} \text{ mol L}^{-1}$ for Pb(II) and constant pH ~5.5 were chosen for studying most of the parameters in present investigation.

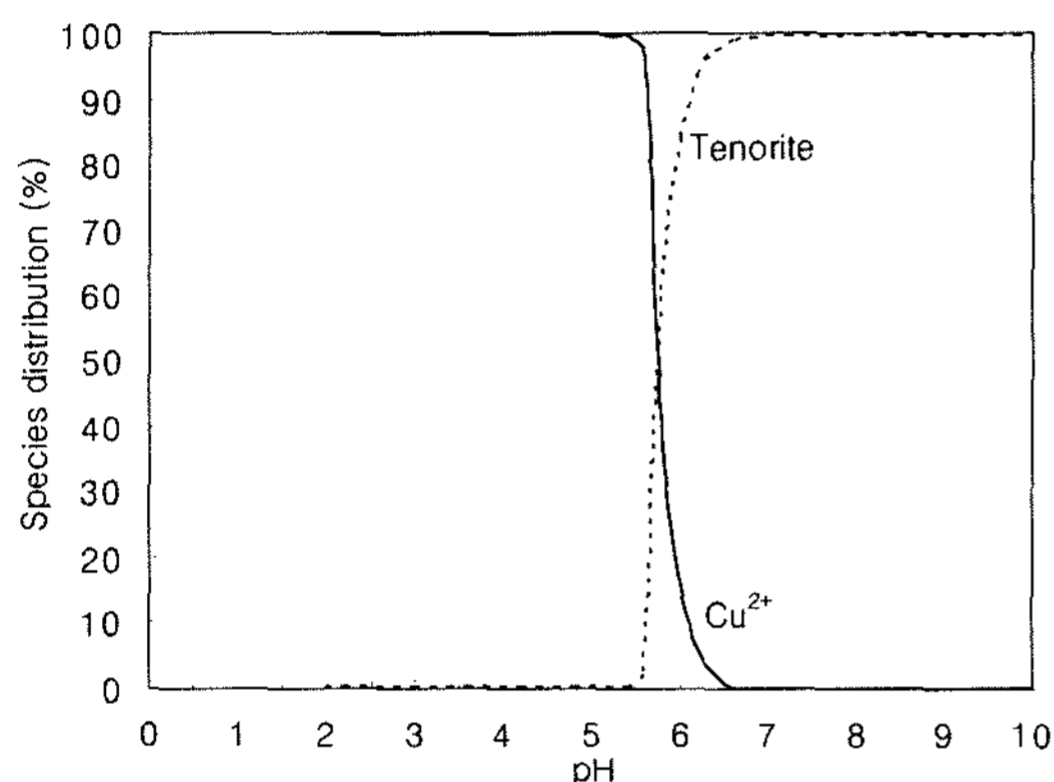


Figure 1. Percentage distribution of various species of Cu(II) as a function of pH [Cu(II) concentration : $3.15 \times 10^{-4} \text{ mol L}^{-1}$].

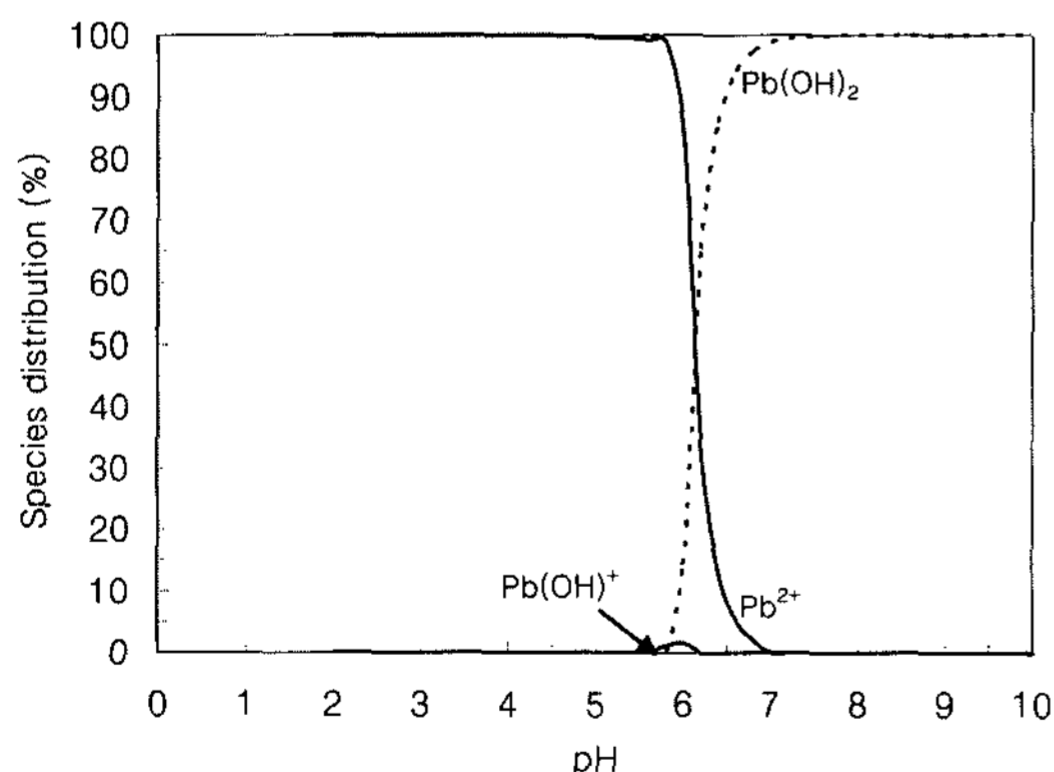


Figure 2. Percentage distribution of various species of Pb(II) as a function of pH [Pb(II) concentration : $1.93 \times 10^{-4} \text{ mol L}^{-1}$].

Time Variation of Adsorption

Study has been carried out with the variation of contact time for the adsorption of Cu(II) and Pb(II) on the surface of sericite keeping the solution ionic strength ($0.001 \text{ mol L}^{-1} \text{ NaNO}_3$) and pH ~5.5 as constant and the initial sorptive concentration 20 mg L^{-1} . Results obtained are

returned in Figure 3, which clearly shows that a fast initial uptake slows down with the lapse of time and an apparent equilibria is to be achieved within ca 10 mins (for Cu(II)) and ca 90 mins (for Pb(II)) between the solid/solution interface. No further adsorption could take place as being checked even after 24 hrs of contact. This clearly suggests that the adsorption of metal cations on the surface of sericite could take place in a single step and not with any complexity.²³⁾ Nevertheless it is possible that during the initial stage of the process, the surface coverage is low and adsorptive ions occupy active surface sites rapidly in a random manner as a result of this the rate of uptake is higher. As time lapses the surface coverage is increased, the rate of uptake becomes slower in latter stages and ultimately almost a plateau region is attained when surface become saturated.²⁴⁻²⁵⁾

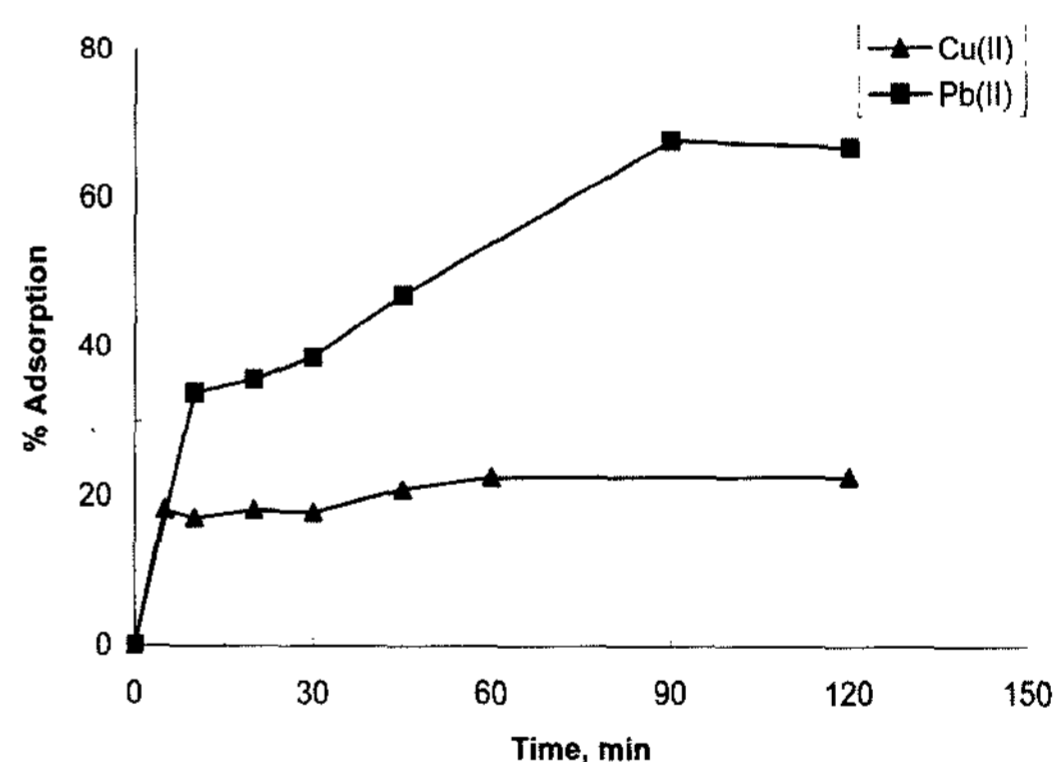


Figure 3. Percentage adsorption of Cu(II) and Pb(II) on the surface of sericite as a function of contact time [Initial sorptive concentration: 20 mg L^{-1} ; Ionic strength: 0.001 mol L^{-1} ; pH~5.5].

Sorptive Concentration Dependence Study

Concentration dependence study has been carried out by changing the sorptive concentration from 1 to 14 mg L^{-1} (for Cu(II)) and 1 to 40 mg L^{-1} (for Pb(II)) at constant ionic strength ($0.001 \text{ mol L}^{-1} \text{ NaNO}_3$) and temperature 25°C . Results obtained for these two cations are plotted between the amounts adsorbed (q ; mg g^{-1}) vs the equilibrium bulk concentration (C_e ; mg L^{-1}) and are shown in Figures 4 & 5. It is

to be noted that with the increase in sorptive concentration the amount adsorbed increases and almost a constant value achieved at higher concentration, this may be explicable as the adsorbent sites eventually become saturated with adsorbed ions and at this stage further addition of sorptive ions would not be expected to increase the amount adsorbed significantly.²⁶⁻²⁷⁾

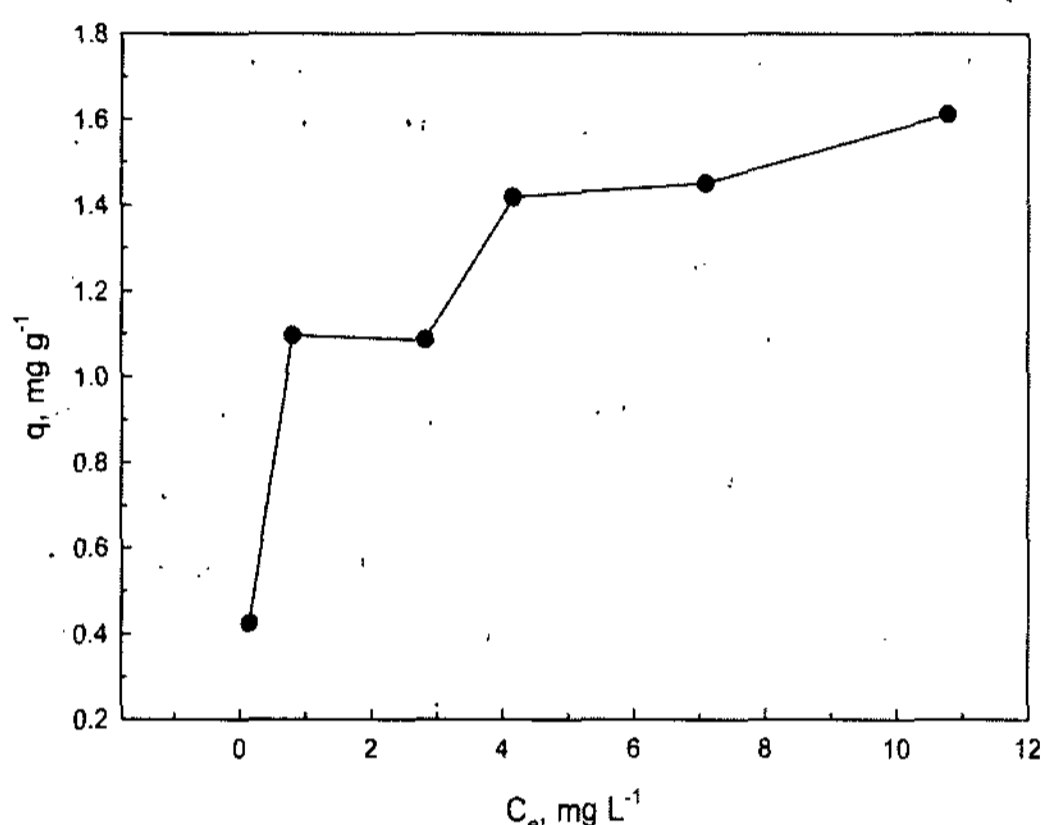


Figure 4. Amount of Cu(II) adsorbed on the surface of sericite with the bulk sorptive concentration [Ionic strength : 0.001 mol L⁻¹ NaNO₃; pH~5.5].

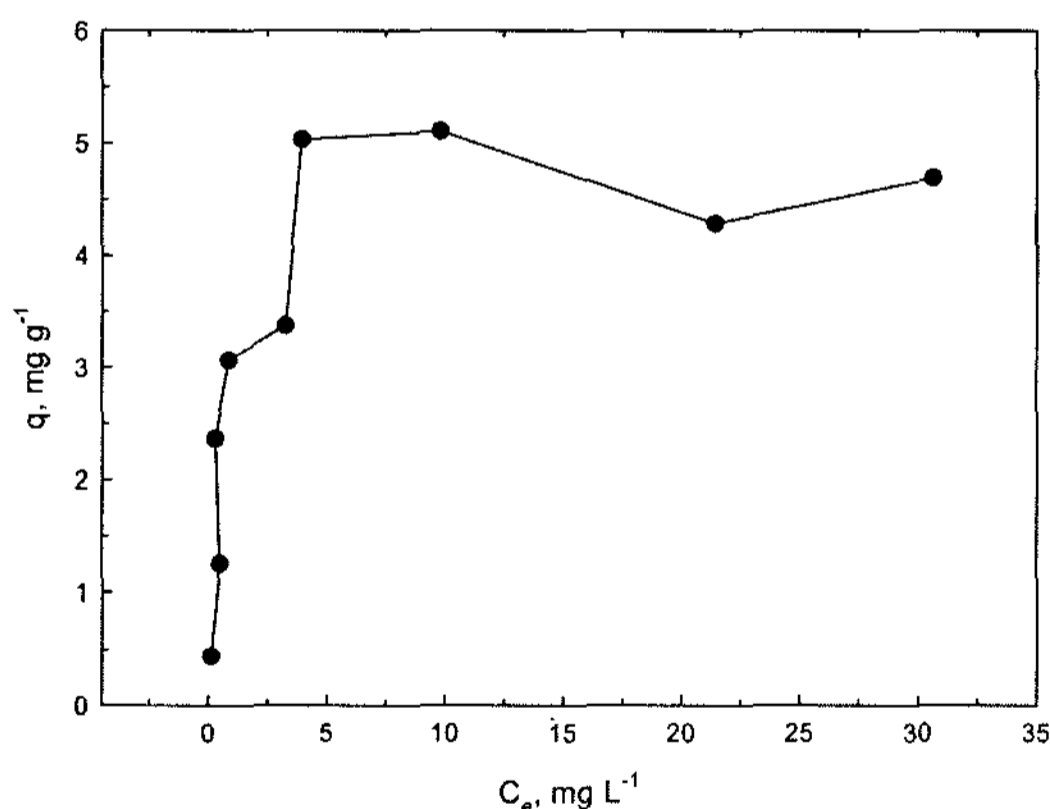


Figure 5. Amount of Pb(II) adsorbed on the surface of sericite with the bulk sorptive concentration [Ionic strength : 0.001 mol L⁻¹ NaNO₃; pH~5.5].

Adsorption Isotherm

The Langmuir adsorption model with its usual form has been adopted for the estimation of maximum metal uptake (q_0) at different initial metal concentrations:

$$\frac{1}{q} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \quad (1)$$

where q is the amount of solute adsorbed per unit weight of adsorbent (mg g⁻¹); C_e is the equilibrium bulk concentration (mg L⁻¹); q_0 is the Langmuir monolayer adsorption capacity i.e., the amount of solute required to occupy all the available sites in unit mass of sericite (mg g⁻¹) and b is the Langmuir constant (L g⁻¹). Fairly good straight lines were obtained while plotting the lines between C_e/q vs C_e (i.e., the reciprocal plot of Figure 6) clearly suggests the applicability of Langmuir adsorption model and it infers that the interactions of metal ions to sericite surface are chemical in nature. The reciprocal of the slopes were obtained to find out the maximum adsorption capacity (monolayer adsorption capacity) for these two ions and these are found to be the 1.674 and 4.697 mg g⁻¹ respectively for Cu(II) and Pb(II) onto the surface of sericite. While making comparison with other commonly used adsorbents, it seems that sericite has relatively lower adsorption capacity (cf Table 2), however the efficiency can be achieved by using cascade arrangements in real wastewater treatment. Similarly, the Langmuir constant 'b' was also estimated and these are found to be 1.289 and 1.626 L mg⁻¹ respectively for Cu(II) and Pb(III). The Langmuir constant 'b' can serve as an indicator of an

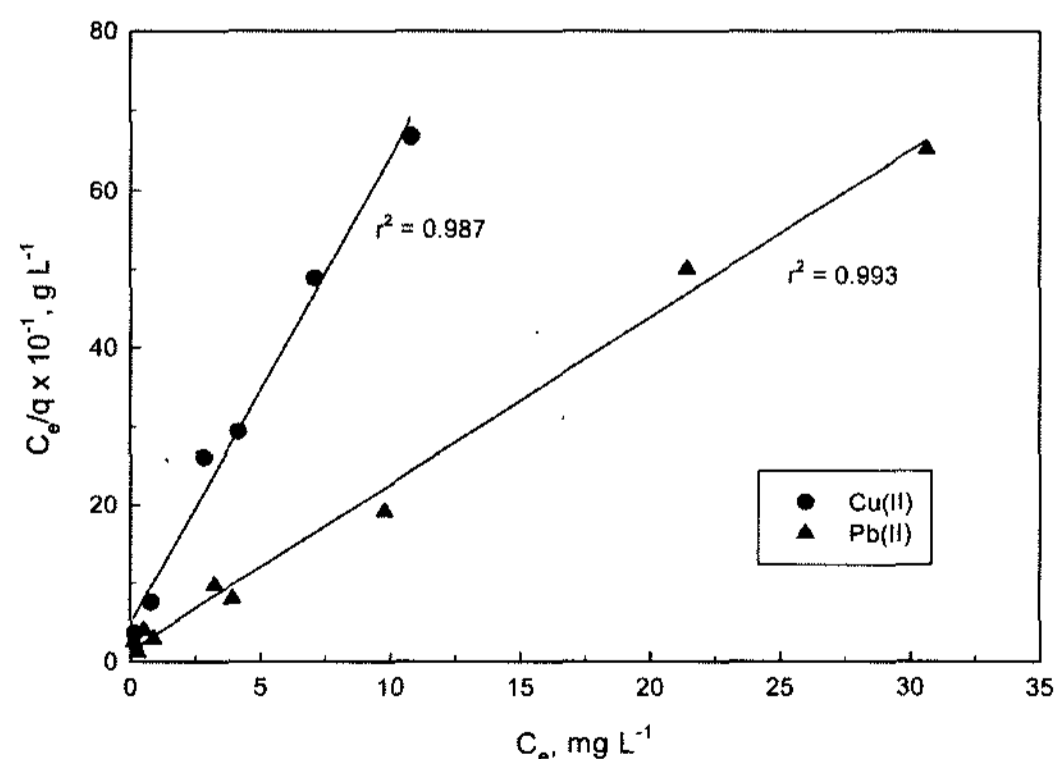


Figure 6. Langmuir adsorption isotherm for Cu(II) and Pb(II) at various sorptive concentrations [Ionic strength: 0.001 mol L⁻¹; pH~5.5].

Table 2. Comparison of Langmuir adsorption capacity of sericite for Cu(II) and Pb(II) with other adsorbents

Adsorbent	Adsorption Capacity (mg g ⁻¹)		Ref.
	Cu(II)	Pb(II)	
Sericite	1.674	4.697	Present Work
Granular Activated Carbon (Coconut shell)	3.558	10.774	Ref. 28
Kaolinite	4.4		Ref. 11
Montmorillonite	28.8		
Granular Activated Carbon (GAC)		10.77	Ref. 29
OXI-GAC (Oxidized activated carbon)		49.728	
ZnO-GAC (Zinc oxide loaded GAC)		331.52	
Coal fly ash prepared Zeolite	50.45		Ref. 30
Commercial Zeolite	53.45		Ref. 31
Natural Zeolite	8.968		
Clay (Kaolinite Based)	1.589		Ref. 16

isotherm rise in the region of lower metal concentrations, which reflects the strength and affinity of the adsorbent for the solute.³²⁾ Also it relates to the equilibrium constant of the process: Cu(II)/or Pb(II) + Sericite = Cu(II)/or Pb(II)...Sericite (Surface adsorption complex).

Relatively higher value of 'b' for Pb(II) again confirms its higher affinity towards the sericite surface.

Further, the results on the steady-state values of sorption of these two cations on sericite surface at various sorptive concentrations were also analyzed using the Freundlich adsorption isotherm in its usual logarithmic form (Equation 2):

$$\text{Log } q = \frac{1}{n} \text{Log } C_e + \text{Log } K_f \quad (2)$$

where q and C_e are the amount adsorbed (mg g⁻¹) and bulk concentration (mg L⁻¹) at equilibrium respectively. K_f and $1/n$ are the Freundlich constants, respectively referred to "adsorption capacity" and "adsorption intensity". While plotting the lines between $\text{Log } q$ vs $\text{Log } C_e$ an almost non-linearity has been observed as the r^2 values lies between 0.887 to 0.687 (cf Table 3) which clearly suggest the non-applicability of

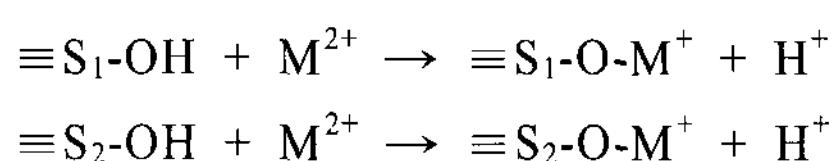
Freundlich model. However, the Freundlich constants were optimized with these lines and these coefficients are returned in Table 3.

 Table 3. Freundlich coefficients for the adsorption of Cu(II) and Pb(II) on sericite [Ionic strength: 0.001 mol L⁻¹ NaNO₃; pH~5.5]

Kf (mg g ⁻¹)		1/n		r ²	
Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
0.868	2.056	0.291	0.339	0.887	0.687

pH Dependence Study

In order to obtain the mechanistic aspects involved at solid solution interface, study has been planned to obtain the pH dependence data at constant sorptive concentration (20 mg L⁻¹) and, constant ionic strength (0.001 mol L⁻¹ NaNO₃). Results obtained are shown graphically in Figure 7, which enables that with increasing the solution pH caused for increase in metal uptake. The surface of the sericite is likely to behave somewhat different as compare to the usual metal oxide surface for adsorption of metal cations. It is to be noted that mainly it contains silanol (via SiO₂ ca 70 %) and aluminol (via Al₂O₃ ca 18%) groups and they are likely to play important role in adsorption/uptake process. Hence, the surface of sericite may behave as two different surface active sites, which is responsible for adsorption.¹⁶⁾ It may be arbitrarily assigned as ≡S₁-OH site, mainly constitute with the silanol group and is become negatively charged at lower pH range (pH ca 2 to 3; near to the p_{ZPC} value of silanol), which facilitate the sorption of metal cations in this pH region. Hence, we observed relatively a higher uptake even at low pH ranges. Further, the second surface site, i.e., ≡S₂-OH represents mainly for aluminol group, which becomes negatively charged at around pH~6, further facilitate for the uptake of metal ions on the surface of sericite. Schematically, we represent the surface behavior for metals cations (M²⁺) as given below:



Moreover, on further increase in pH (i.e., beyond 7) there might be a mixed effect of adsorption and co-precipitation of metals ions on the surface. Hence, caused for apparently very high uptake of metal ions in this pH region.

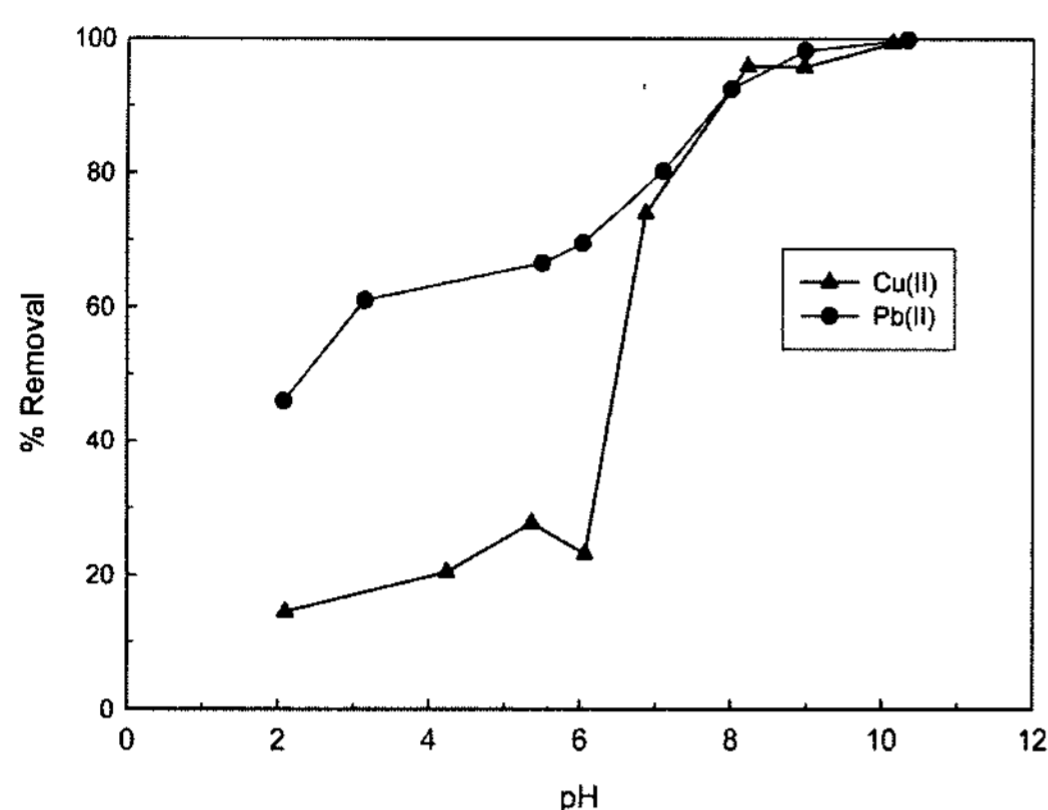


Figure 7. Effect of pH on the removal of Cu(II) and Pb(II) on the surface of sericite [Initial Cu(II) and Pb(II) concentration: 20 mg L⁻¹; Ionic Strength : 0.001 mol L⁻¹ NaNO₃].

Effect of Ionic Strength

The change in ionic strength (from 0.001 to 0.1 mol L⁻¹ NaNO₃) has been assessed for the adsorption of Cu(II) and Pb(II) on the surface of sericite at constant sorptive concentration: 20 mg L⁻¹ and pH~5.5. Results obtained are returned in Figure 8, which clearly shows that while increasing the ionic strength the uptake of metal cations slightly suppressed. Quantitatively, the increase in ionic strength from 0.001 to 0.1 mol L⁻¹ NaNO₃ (i.e., 100 times) the uptake of metal ions decreases only ca 11% for Cu(II) and ca 26% for Pb(II). Traditionally, the ionic strength dependence of metal ions removal from solution by soil minerals is used to distinguish between non-specific and specific adsorption. Outer sphere complexes involve only electrostatic interaction and are strongly affected by the ionic strength of the aqueous phase, while inner sphere complexes involve much stronger covalent or ionic binding and are only weakly affected by the ionic strength.³³⁾ Hence, we conclude

that the uptake of metal cations by sericite mainly proceeds through inner-sphere-complexation as it is not greatly affected by the 100 fold increase in ionic strength.

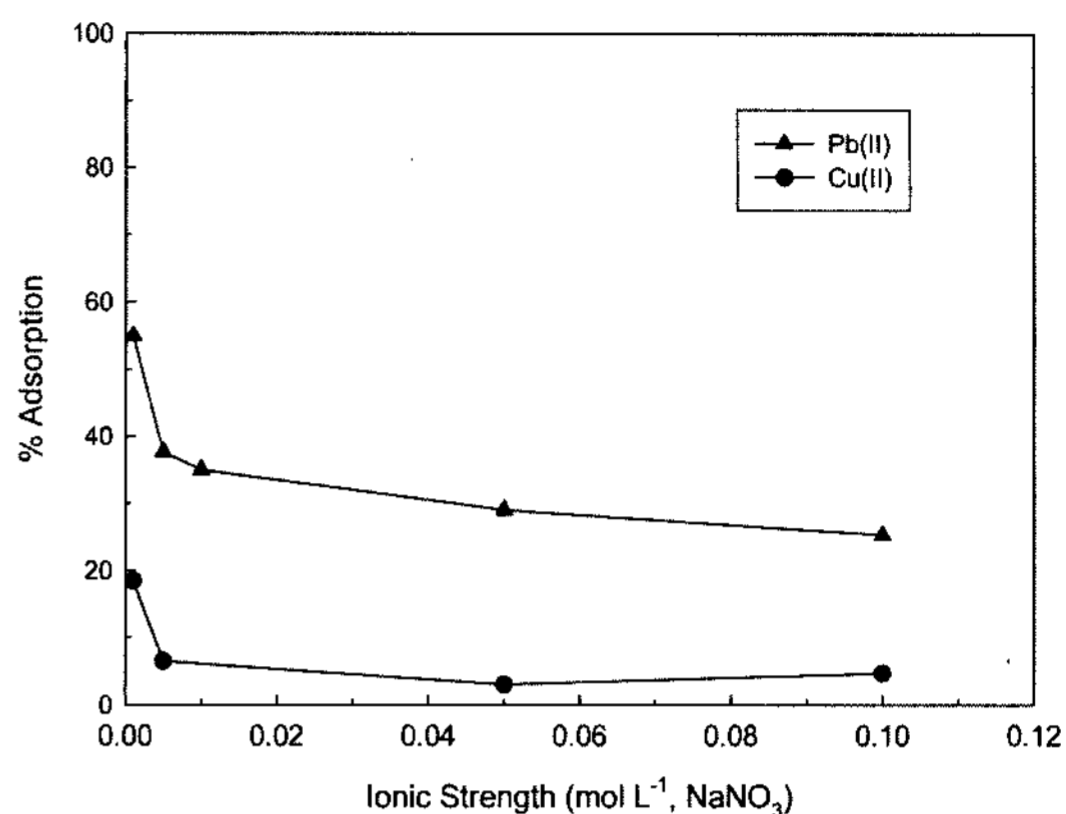


Figure 8. Variation of percentage adsorption of Cu(II) and Pb(II) on the surface of sericite as a function of ionic strength [Initial sorptive concentration : 20 mg L⁻¹; pH~5.5].

CONCLUSIONS

The possible application of sericite in wastewater treatment has been assessed as it applied for the removal of Cu(II) and Pb(II) from aqueous solutions. Batch type experiments performed reveals that sericite can be used as an alternative sorptive material for the removal of these two heavy metal toxic ions from aqueous solutions. Adsorption data obtained for these two cations were explained well for Langmuir adsorption model rather than Freundlich model and the adsorption capacity obtained were found to be 1.674 and 4.697 mg g⁻¹ respectively for Cu(II) and Pb(II). The inner-sphere adsorption of Cu(II) and Pb(II) on sericite was found to be increased with solution pH and sorptive concentration.

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