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Application of pyrophyllite mine waste for the removal of cadmium and lead ions from aqueous solutions

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ABSTRACT

The application of pyrophyllite mine waste as a low-cost adsorbent for the removal of cadmium and lead ions from aqueous solution has been investigated. Silica and alumina are found to be the two major constituents of pyrophyllite waste. Experimental conditions in terms of shaking time, pH, amount of adsorbent, metal ion concentration, and temperature have been optimized for the maximum uptake of cadmium and lead ions. It has been observed that 75% of cadmium and 98% of lead ions could be removed at acidic pH within 30 min of equilibrium time. The experimental data are analyzed by the Freundlich and Langmuir isotherm models. The thermodynamic parameters such as ΔG°, ΔH°, and ΔS° indicate the effectiveness of pyrophyllite waste to remove cadmium and lead ions from aqueous solution. The positive value of ΔH° indicates that the adsorption process is endothermic in nature. The kinetics of adsorption is best fitted by a pseudo-second-order equation. The Fourier transform infrared, field emission scanning electron microscope, and X-ray photoelectron spectroscopy studies have been conducted to confirm the adsorption of cadmium and lead ions on pyrophyllite waste.

Keywords: Adsorption; Pyrophyllite waste; FTIR; FESEM; XPS; Cadmium; Lead; Freundlich isotherm; Thermodynamic parameter; Kinetics

1. Introduction

Cadmium and lead are toxic metals and found in several industrial discharges and effluents. Several industrial processes such as alloys, soldering materials, electroplating, batteries, dyes, pesticides, and textile industries release cadmium ions into the aquatic system. Similarly, the primary sources of human exposure to lead include lead mining, lead smelting, lead-based paint, lead-containing pipes, coal combustion, automobile emissions, gasoline, and sewage waste water. All these sources contribute to making the water toxic. The harmful effects of cadmium and lead ions when present in water possess hazardous to human life, are well documented in several literatures [1–5]. The permissible limits of lead and cadmium ions for human consumption are 0.01 and 0.02 mg/L, respectively [6,7]. As the presence of any toxic metal ions in wastewater is a serious environmental concern, it is necessary to remove these ions, before discharging it into the natural water stream.

There are several methods such as precipitation, ion exchange, and adsorption that can treat metal-contaminated effluents and wastewater. However, the

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selection of any treatment method is based on the concentration of pollutants and the cost of treatment. Adsorption is one of the low-cost methods for the removal of heavy metal ions from the aqueous systems. Removal of lead and cadmium ions from the aqueous system by the use of several minerals and industrial by-products as adsorbents has been carried out due to their low cost, availability, and adsorbing capacity. Clay, goethite, hydroxyapatite, calcite, slags, sludges, dolochar, etc. have been studied in the removal of heavy metal ions [8–12]. The presence of different surface functional groups, pores, and cavities present in these industrial wastes are responsible for the adsorption of heavy metal ions.

Pyrophyllite is an important industrial mineral used for different industrial applications such as slate, pencils, tailors chalk, gasket material, ceramics, tiles, bricks, glass, fiber plastic, etc. It is composed of aluminum and silicate hydroxides ($Al_2Si_4O_{10}(OH)_2$). The market price of pyrophyllite in many pottery, ceramic, and tile industries directly depends on its Al_2O_3 content, the presence of impurities like iron, and the high degree of whiteness. However, large amounts of waste materials containing appreciable quantities of pyrophyllite are being generated while mining the pyrophyllite ore. The accumulation of this waste material in the mines site is increasing every year. Some useful investigations carried out on pyrophyllite waste material by different investigators are in the preparation of ceramic tiles, stabilization and neutralization of pyrophyllite mine wastes, adsorption of humic acids, etc. [13–15]. Some investigations are also carried out by using pyrophyllite as an adsorbing material. The studies on the separation of cyanide ions from aqueous solutions by the pyrophyllite have indicated the removal of ~99% cyanide ions. The adsorption of cyanide ions increases with a rise in temperature [16]. The adsorption of cationic and anionic dyes from aqueous solution has shown that, pyrophyllite in water, exhibits a negative surface charge within the pH 2–12. The negative hydrophilic surface sites of pyrophyllite are responsible for the adsorption of cationic dye molecules. The adsorption of anionic dye is possible after a charge reversal of pyrophyllite by the addition of trivalent cations [17]. Batch adsorption study has been carried out to remove excess fluoride ions from water by using pyrophyllite as an adsorbent. The studies indicated the removal of ~85% fluoride ions within 2 h of contact time at an adsorbent dose of 4 g/L from the initial fluoride concentration of 10 mg/L. The maximum adsorption of fluoride takes place at pH 4.9 [18]. In some instances, the pyrophyllite surface modified with organic molecules such as 3-(2-aminoethylamino) propyl-methyldimethoxysilane has been investigated as an adsorbent for the removal of lead ions from aqueous solutions [19].

In the present study, the removal of cadmium and lead ions from aqueous solutions using pyrophyllite waste as an adsorbing material has been undertaken for the adsorption studies. The adsorption characteristics of pyrophyllite waste have been examined by investigating the effect of certain parameters such as contact time, pH, amount of initial lead and cadmium concentration, and amount of adsorbent to optimize the removal process.

2. Materials and methods

2.1. Adsorbent

Pyrophyllite waste samples were collected from mines near Agra, Uttar Pradesh, India. The material was washed several times with deionized water to remove contaminants and then dried at 50°C for few hours. The material was then subjected to fine grinding using laboratory ball mill with required balls to particle ratio. The samples of different particle sizes, viz 75, 100, 210, 300, and 500 micron size, were prepared for the adsorption studies.

2.2. Adsorbate

Anhydrous cadmium chloride and lead nitrate (Analytical grade) were used without any purification. Stock solutions of cadmium and lead (1,000 mg/L) were prepared by dissolving the required amounts of the compound in distilled water. Different concentrations of these two solutions were then prepared by progressive dilution of the stock solution. The pH of the solution was adjusted to the required value by adding either dilute H_2SO_4 or NaOH solutions.

2.3. Adsorption method

The batch adsorption experiments were carried out in 250 mL conical flasks in a solution of cadmium and lead in various concentrations (5–60 mg/L). The samples with different particle sizes were added to the 100 mL of cadmium and lead solutions. The solutions were agitated by a magnetic stirrer for the desired time period. At the end of the required time interval, the solutions were filtered using Whatman 42 filter paper and the pH of the final solution was measured. Adsorption experiments were carried out by varying different variables such as agitation time, metal ion concentration, pH, adsorbent dosages, and temperature. Kinetic studies at different temperatures were performed for an initial concentration of 30 mg/L. The resultant filtrates collected at the end of the predetermined time intervals were subjected to the determination of lead and cadmium ions.

2.4. Analytical methods

The cadmium and lead concentrations in the solution at equilibrium were analyzed using Perkin Elmer-2380 Atomic absorption spectrophotometer (AAS). Fourier transform infrared (FTIR) spectra of the samples were recorded on a Shimadzu FTIR by using KBr as reference. Scanning electron microscope (SEM) studies of pyrophyllite sample, pyrophyllite adsorbed with cadmium and lead were analyzed by Hitachi 3400 N SEM.

2.5. Desorption studies of cadmium and lead ions

Desorption of both cadmium and lead ions from loaded pyrophyllite waste adsorbent was performed using water and two concentrations of hydrochloric acid (HCl) solution. Studies were carried out by exposing the loaded samples separately to 100 mL solution of 0.1 and 0.2 N HCl. The mixture was agitated at 500 rpm for different intervals of time. At the end of desorption time, the pyrophyllite samples were separated by decantation and filtration. The concentrations of cadmium and lead ions were measured in the filtrate by AAS techniques.

3. Results and discussion

The pyrophyllite sample contains 49.38% SiO_2, 23.96% Al_2O_3, 9.8% K_2O, 1.8% Fe_2O_3, and 1.35% Na_2O. The sample also contains 3.90% CaO, 1.96% MgO, and 5.20% Loss on ignition. Pyrophyllite samples, in general, contain quartz, muscovite, and orthoclase with intergranular spaces within the silicates. The X-ray diffraction studies of the present sample carried at Co kα radiation is shown in Fig. 1. The sample contains goethite, kaolinite, muscovite, orthoclays, and pyrophyllite as the associated mineral phases in this waste material. It is seen that these minerals and the voids present in pyrophyllite are responsible for the adsorption of different metal ions [20].

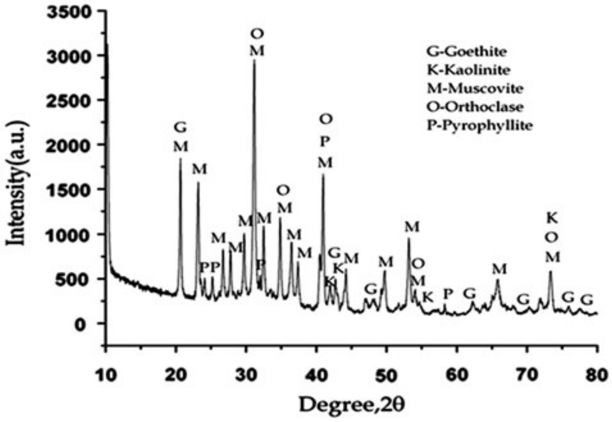

Fig. 1. X-ray diffraction patterns of potash pyrophyllite samples.

Various adsorption parameters for the effective removal of cadmium and lead ions using pyrophyllite as an adsorbent from the aqueous solution were studied and optimized. The adsorption concentration of divalent metal ions on pyrophyllite sample was obtained by calculating the difference between the initial and final concentration in solution. The adsorption capacity q (mg/g) of both metal ions on pyrophyllite was calculated as:

$$q = (C_0 - C_t)V/M \tag{1}$$

where C_0 (mg/L) is the initial metal ion concentration, C_t (mg/L) is the metal ion concentration at any time t (min), V (L) is the volume of the solution, and M (g) is the weight of adsorbent used. The adsorption capacity of the pyrophyllite was determined by changing various physical and chemical parameters.

3.1. Effect of particle size and contact time

The effect of particle size and shaking time on the adsorption behaviors of Cd(II) and Pb(II) into pyrophyllite was studied. The particle size of pyrophyllite was varied from 75 to 500 μm while the equilibrium time was varied in the range of 4–120 min. Fig. 2 shows the Pb(II) and Cd(II) uptake capacity at different particle sizes and shaking time. Adsorption studies were carried out by using 100 mL solutions at an initial metal ion concentration of 30 mg/L and 1.0 g of pyrophyllite sample. It was observed that the adsorption capacity of Cd(II) and Pb(II) ions decrease with an increase in particle diameter. As the adsorption is a surface phenomenon, it is very likely that the extent of adsorption is proportional to the surface area. Hence, smaller the particle size greater will be the amount of adsorption due to their larger surface area [12]. Hence, further adsorption studies were carried out at lower particle size only. It is also observed from the figure that the adsorption capacity of pyrophyllite with regard to Pb(II) ions is much high compared to Cd(II) ions.

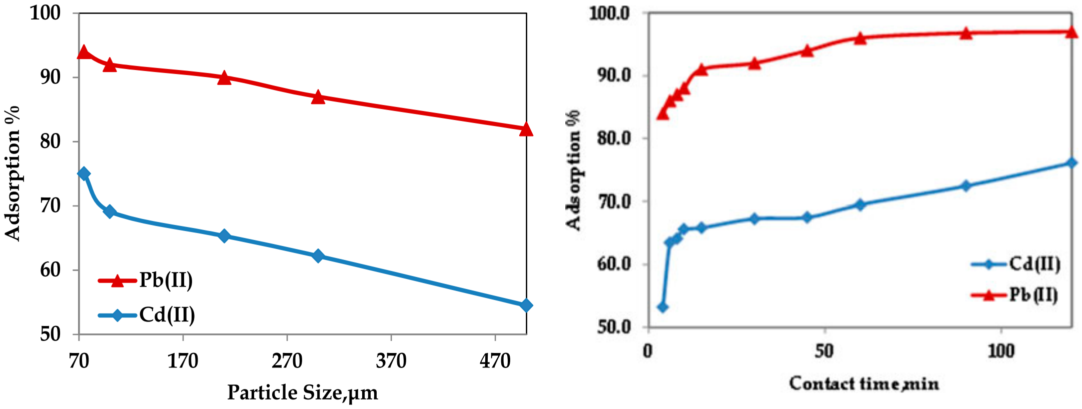

Fig. 2. Adsorption of pyrophyllite on cadmium and lead ions varying particle size and contact time.

Under the similar conditions, cadmium and lead uptake capacity of the pyrophyllite at different times of shaking time is shown in Fig. 2. It is observed that in case of Cd(II) ions, the adsorption of metal ions is faster during the initial period followed by a period of the slower rate. However, there is a high intake of Pb (II) ions even after two minutes of shaking time. It may be explained that initially all sites on the adsorbent surface are vacant and the solute concentration gradient is relatively high [21].

3.2. Effect of adsorbent dosage and pH

The adsorbent dosage is an important parameter with respect to the adsorption studies as it determines the potential of a material to adsorb the metal ions for a given concentration of the sorbent. The influence of the amount of pyrophyllite on the adsorption of Cd(II) and Pb(II) ions was investigated. The solution concentration of 30 mg/l of metal ions, particle size of 100 micron was taken during the course of the experiments. The amount of pyrophyllite varied from 0.25 to 2 g and was shaken for 30 min. The experimental results of the studies as shown in Fig. 3 indicate that the adsorption values increase with an increase in the amount of pyrophyllite dosage. It attained the maximum value at 1 g of pyrophyllite, which remains almost constant up to 2 g of pyrophyllite. As a result, 1 g of pyrophyllite was sufficient for the adsorption and used in all the subsequent studies.

The effect of pH on the adsorption of Cd(II) and Pb(II) was investigated by varying the pH from 2 to 10. The result of the studies on the uptake capacity of Cd(II) and Pb(II) is also shown in Fig. 3. In the case of Cd(II), the adsorption of cadmium ions increased from 7 to 66% but in the case of Pb(II), it varied from 32 to 95%. The optimum pH for the maximum removal of Cd(II) ions is found to be at pH 6.3 and that for lead is 5.5. Hence, it was concluded that slight acidic pH is found to be favorable for adsorption of both the metal

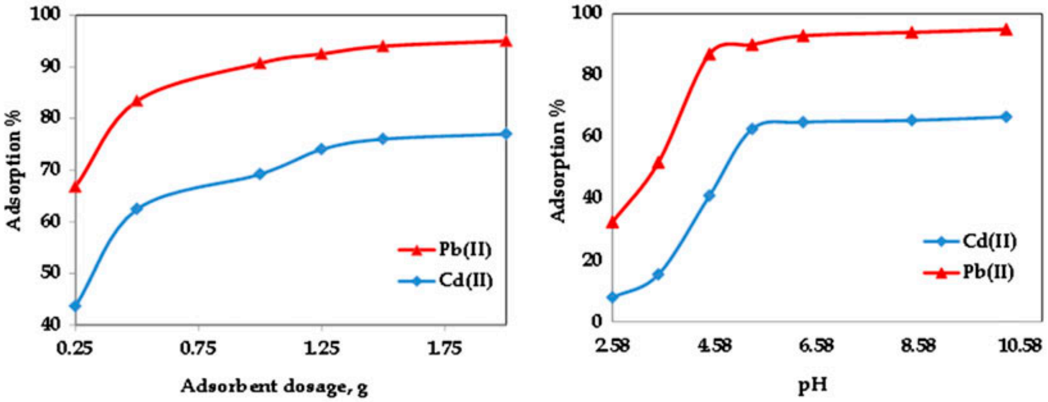

Fig. 3. Adsorption of pyrophyllite on cadmium and lead ions varying adsorbent dosage and pH.

ions. Several investigators have suggested that in the case of oxide minerals, the variation of adsorption is less at $\mathrm{pH} < 4$ whereas the adsorption is maximum in pH 4–8. Beyond this pH value, the adsorption capacity remains constant.

3.3. Effect of temperature and initial concentration of cadmium and lead ions

The temperature dependence of Cd(II) and Pb(II) adsorption by pyrophyllite was studied with a constant initial metal ion concentration of 30 mg/L for different temperatures (300, 313, 333, 353, and 373 K). The results of the studies are shown in Fig. 4. It has been observed that the adsorption (%) increases with the increase in temperature in both the cases due to the increased penetration of divalent ions inside the pores of pyrophyllite at higher temperature. Fig. 4 also shows the effect of varying concentrations of cadmium and lead ions on the adsorption under the optimized conditions of 30 min shaking time and 1 g of adsorbent in the aqueous medium. The concentrations of cadmium and lead varied from 5 to 60 mg/L. The results of the studies showed that the adsorption of the cadmium decreases with the increase in the cadmium concentration while lead adsorption remains constant up to 30 mg/L and then slightly decreases. The results indicated that the pyrophyllite surface is fully saturated and unavailable for further adsorption of metal ions.

3.4. Adsorption isotherms

The data concerning the extent of adsorption with the increase in cadmium and lead ion concentration was subjected to the examination of Freundlich model isotherms equations.

The Freundlich equation was used in the form,

$$q_e = K_F C_e^{1/n} \qquad (2)$$

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

where q_e is the equilibrium concentration of cadmium and lead ions on pyrophyllite, C_e is in the equilibrium concentration of cadmium and lead remaining in the solution. K_F and n are parameters, characteristic of the adsorbent–adsorbate system.

The Freundlich plot of log q_e versus log C_e is shown in Fig. 5. The numerical values of adsorption capacity (K_F) and intensity ($1/n$) were calculated from the intercept and slope of the straight line using a least-square fit program.

If the value of n is 1, it suggests that the partitions between the two phases are independent of the concentration. If the value of $1/n$ is below one, it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates the cooperative adsorption [22]. If $n > 1$, this indicates a favorable sorption process [23]. In the present study, the adsorption value $1/n = 0.96$ while $n = 1.04$ thus obtained from the experimental results show that the sorption of Pb(II) onto pyrophyllite is favorable. The R^2 value is 0.99. Similarly for cadmium ion, the n value of 1.48 and R^2 value of 0.970 also indicates the favorable adsorption.

The Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent [24]. The expression of the Langmuir model is given as,

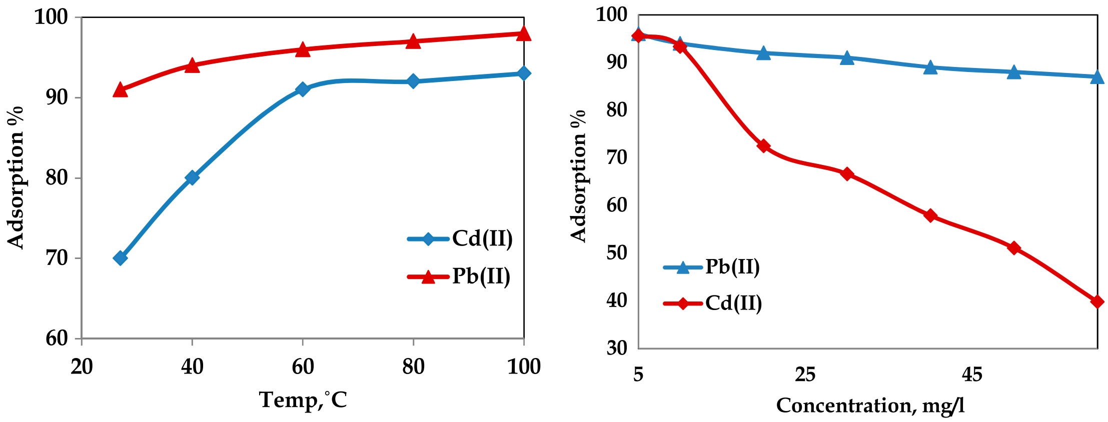

Fig. 4. Adsorption of pyrophyllite on cadmium and lead ions at different temperatures and different concentrations of cadmium and lead ions.

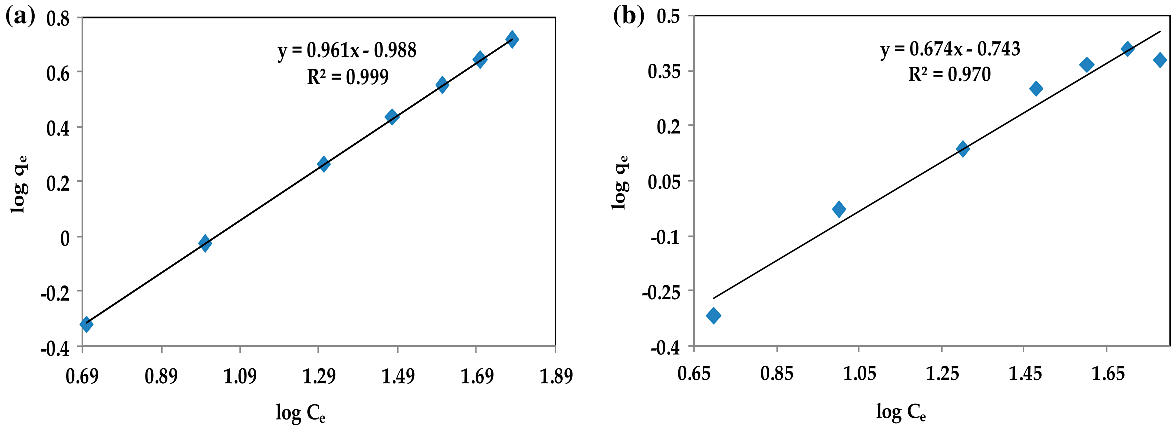

Fig. 5. Freundlich isotherm for lead (a) and cadmium (b) adsorption.

$$q_e = Q_0 K_L C_e/(1 + K_L C_e) \quad (4)$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed pyrophyllite and unabsorbed pyrophyllite concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of the pyrophyllite per unit mass, and K_L is a constant related to the affinity of the binding sites (L/mg).

The Langmuir equation can be described by the linearized form:

$$1/q_e = 1/Q_0 + 1/(K_L C_e Q_0) \quad (5)$$

The linear plot of specific adsorption ($1/q_e$) against the equilibrium concentration ($1/C_e$) (Fig. 6) shows the straight line in both the metal ions indicating that the adsorption obeys the Langmuir model. The Langmuir constants Q_0 and K_L were determined from the slope and intercept of the plot.

The dimensionless separation factor, $R_L = 1/(1 + (1 + K_L C_0))$ value is used to identify the adsorption nature in the study. The adsorption nature is unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$, and irreversible if $R_L = 0$ [25]. In the present study, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. From the current investigation, for lead adsorption study, the maximum monolayer coverage capacity (Q_0) is determined to be 43.47 mg/g, K_L (Langmuir isotherm constant) is 0.002 L/mg, R_L (the separation factor) is 0.48 indicating that the equilibrium sorption is favorable. The R^2 value is 1, proving that the sorption data is fitted well to Langmuir isotherm model. Similarly for cadmium, R_L value being 0.38 also indicates the favorable adsorption. The best-fit equilibrium model was determined on the basis

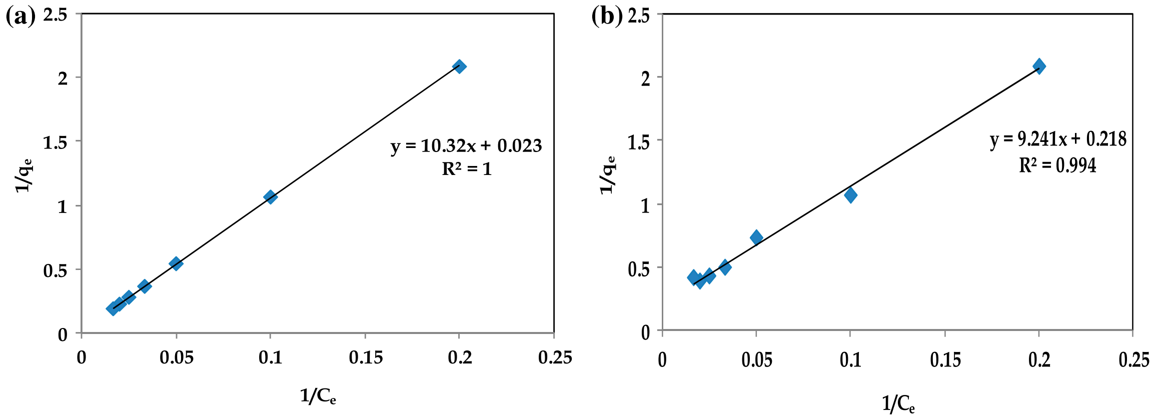

Fig. 6. Langmuir isotherm for lead (a) and cadmium (b) adsorption.

of regression correlation coefficient R, which follows Langmuir isotherm more closely.

3.5. Thermodynamics study

The thermodynamic quantities such as ΔH°, ΔS°, ΔG° of cadmium and lead ions adsorption on pyrophyllite were calculated from the distribution coefficient values using Eqs. (6) and (7). Fig. 7 represents the linear variation of ln K_d with the reciprocal of temperature where the values of ΔH° and ΔS° were computed from the slope and intercept of the straight line.

By applying Van't Hoff equation,

$$\ln K_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \tag{6}$$

where ΔS° is the entropy change for the process. ΔH° is the enthalpy. R is the gas constant, and T is the temperature in absolute scale. The changes in free energy (ΔG°) for the specific adsorption have also been calculated using the equation:

$$\Delta G^\circ = -RT \ln K_d \tag{7}$$

The thermodynamic parameters like ΔG°, ΔH°, and ΔS° were calculated from the adsorption data. It was observed that as the temperature increased from 300 to 373 K, K_d values varies from 0.23 to 1.32 g^{-1}. ΔG° becomes more negative, in both the cases of cadmium and lead, indicating a greater adsorption capacity at higher temperatures [26]. The ΔG° values in the case of cadmium vary from 3.62 to −0.88 kJ/Mol whereas it was completely negative in the case of lead ions (from −0.027 to −4.92 kJ/Mol). The positive value of ΔH° (Cd: 7.82 kJ/Mol and Pb: 7.804 kJ/Mol) confirmed that the process was endothermic in nature. The positive value of ΔS° (Cd: 2.73 kJ/Mol and Pb: 2.32 kJ/Mol) suggested an increase in randomness at solid and solution interface.

3.6. Adsorption kinetics study

A linear form of the pseudo-first-order model is described in the following form [27].

$$\log(q_e - q_t) = ((\log q_e - k_1 t)/2.303) \tag{8}$$

A linear plot of $\log(q_e - q_t)$ against time was plotted for the determination of rate constant and shown in Fig. 8. The first-order rate constant (k_1) for Cd(II) and Pb(II) was found to be 4.14×10^{-5} and 7.36×10^{-5} min^{-1}, respectively. The R^2 value was found as 0.83 and 0.90 for Cd(II) and Pb(II), respectively. It was observed that the pseudo-first-order model did not fit well. The calculated values q_e (Cd: 0.06 mg/g and Pb: 0.07 mg/g) do not agree with the experimental q_e values (Cd: 2.1 mg/g and Pb: 2.73 mg/g) and suggests that the adsorption of both ions does not follow first-order kinetics.

The pseudo-second-order kinetics may be expressed in a linear form as:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \tag{9}$$

The plots of t/q_t versus t are shown in Fig. 9. The values of the calculated and experimental q_e show that there is some connection between q_e experimental (Cd: 2.1 mg/g and Pb: 2.73 mg/g) and q_e calculated values (Cd: 2.2 mg/g and Pb: 2.9 mg/g) for the pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics as compared to first-order.

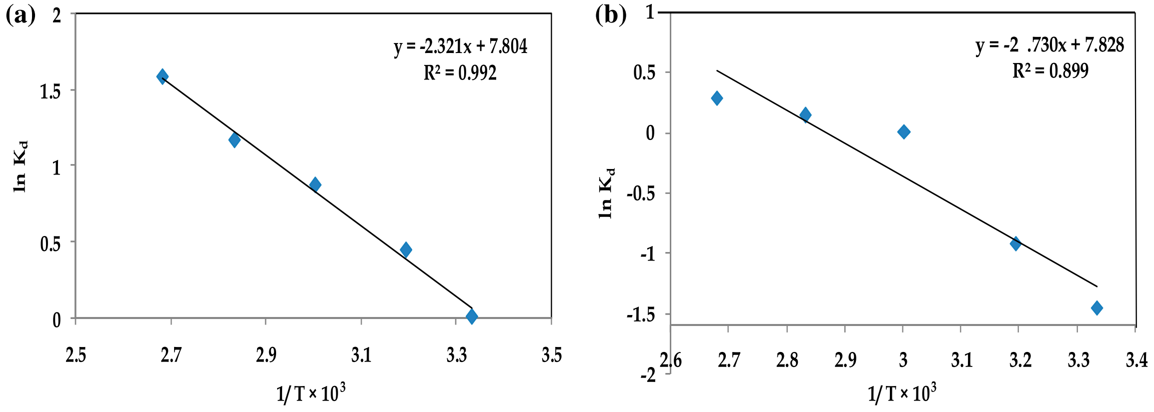

Fig. 7. Plot of ln K_d versus $1/T$ for lead (a) and cadmium (b).

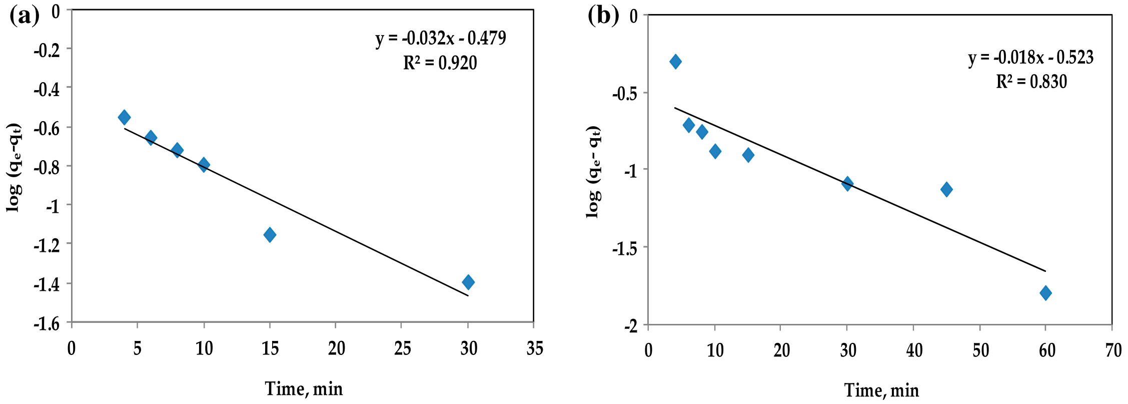

Fig. 8. Pseudo-first-order reaction kinetics lead (a) and cadmium (b).

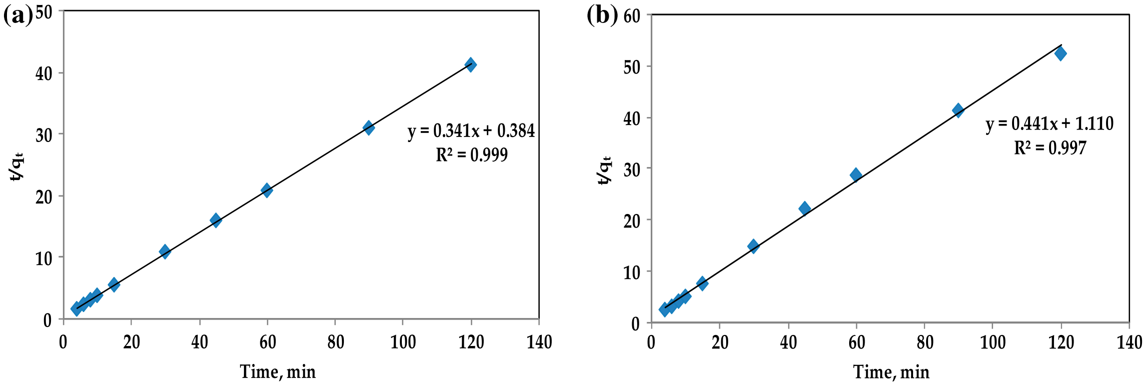

Fig. 9. Pseudo-second-order kinetics lead (a) and cadmium (b).

The adsorption data for cadmium and lead are found to fit well to pseudo-second-order kinetics as the regression coefficients R^2 for both Cd(II) and Pb(II) plot are nearly equal to one. The theoretical as well as experimental q_e value is nearly equal. However, the value of q_e increases with increase in temperature indicating the chemisorptions nature of the adsorption process [28].

4. Mechanism of adsorption (FTIR, FESEM, and XPS studies)

4.1. FTIR studies

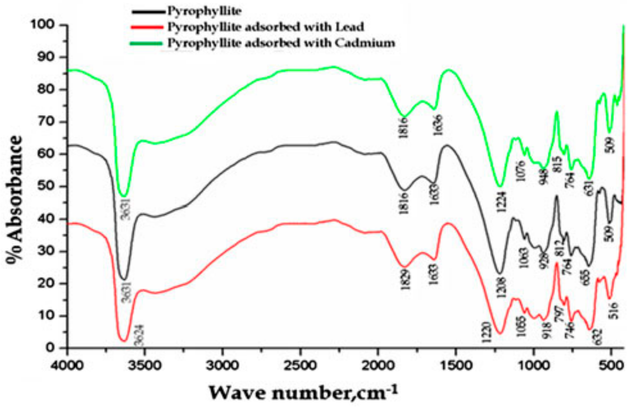

Fig. 10. FTIR spectra of pyrophyllite and adsorbed with cadmium and lead ions.

FTIR studies were undertaken to investigate the adsorption of metal ions by pyrophyllite waste occurred due to the variation in the functional group. The spectra of pyrophyllite adsorbed with metal ions are shown in Fig. 10. In the case of pyrophyllite, the band occurring at 3,631 cm^{-1} is due to O–H stretching vibration of OH groups bonded to Al ions within the layer structure. The band at 1,633 cm^{-1} for pyrophyllite is attributed to the H–O–H deformation of water molecules. The pyrophyllite sample with and without

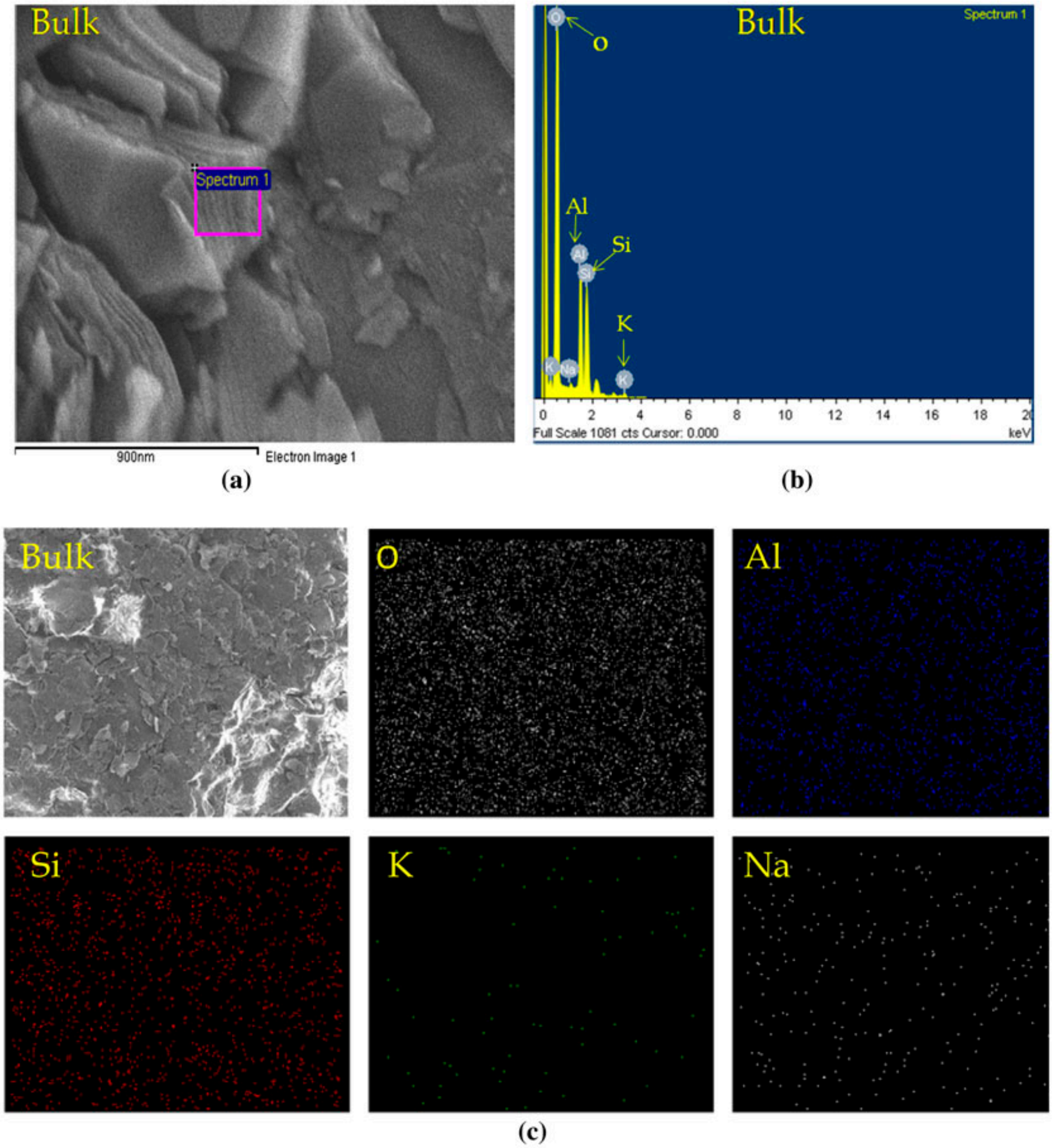

Fig. 11. (a) FESEM-EDX micrographs for potash pyrophyllite (bulk) and (b) EDX (c) mapping of constituent elements Na, K, Si, O, Al in bulk sample.

adsorption (Cd^{++}) has shown spectra at 3,631 and 509 cm^{-1}, respectively, that are due to O–H–O stretching and Si–O bending vibrations. In the case of cadmium adsorption, the band around 1,636 cm^{-1}, assigned to deformation vibration of adsorbed water in the structure of silicate is slightly shifted compared to the original pyrophyllite. The pyrophyllite adsorbed with lead ions showed a peak at 3,624 cm^{-1} (OH–Al in plane) which indicates OH stretching of the inner hydroxyl group. Similarly, the bands near 516, 797, and 918 cm^{-1} are assigned to Al–O–Si, Si–O–Al, and Al–Al–OH deformation vibrations [29–33].

4.2. FE-SEM/EDX analysis

In this present study, field emission scanning electron microscope (FESEM) and Energy dispersive X-ray (EDX) mapping are conducted to evaluate the adsorption of cadmium and lead ions on pyrophyllite surface. Fig. 11(a) shows the FESEM micrographs, EDX mapping of different elements and its corresponding point spectra. Figs. 12 and 13 display the corresponding morphology and elemental mapping after adsorption with cadmium and lead ions, respectively. It is observed that the surface of pyrophyllite showing the

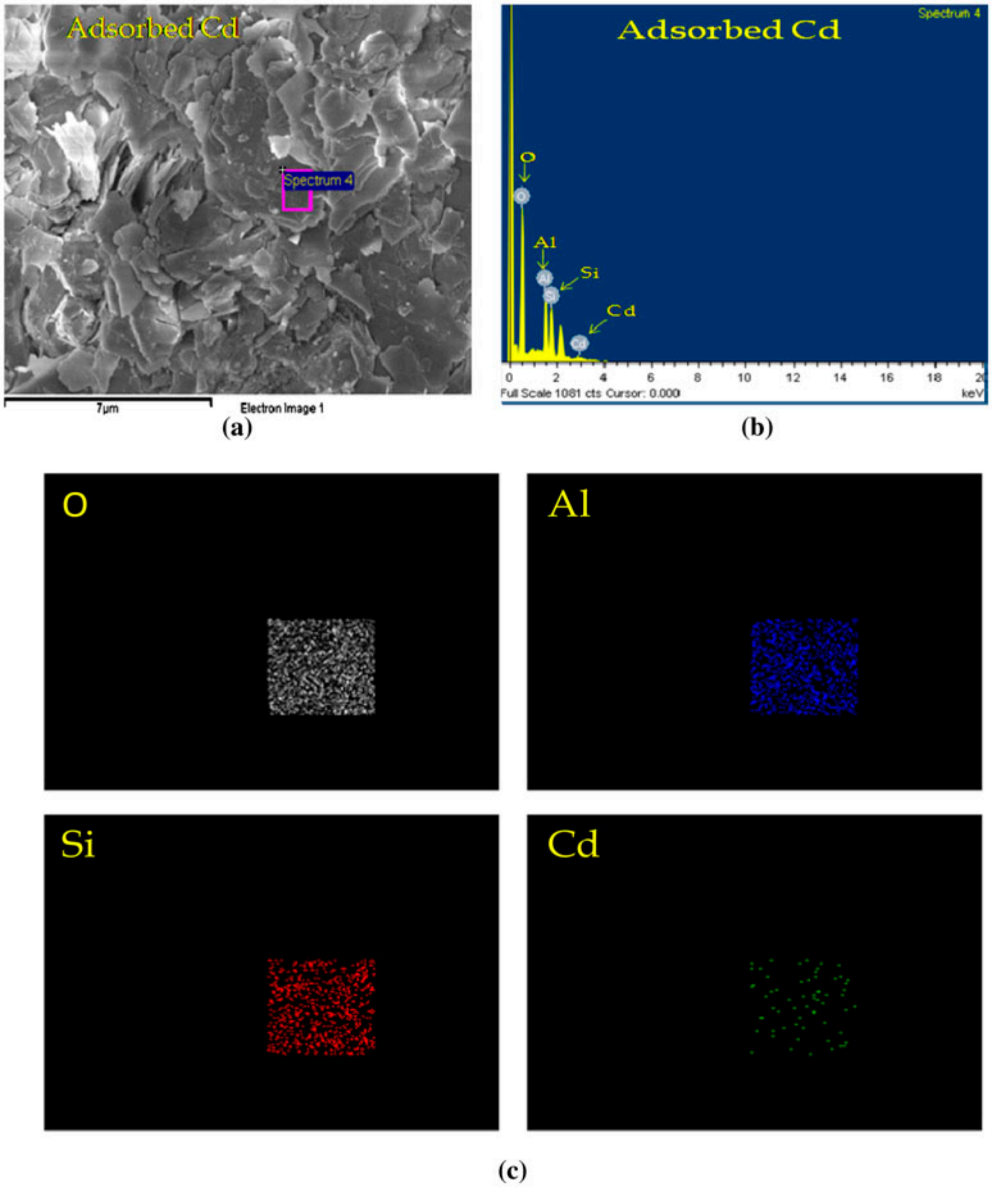

Fig. 12. (a) FESEM-EDX micrographs for cadmium adsorbed surface of pyrophyllite and (b) EDX (c) mapping of constituent elements Si, O, Al, and Cd in adsorbed sample.

lamellar habit consisting of stakes of individual sheet-like or platy crystals held together by van der Waals force of attraction at 23.92 KX magnifications. After adsorption of cadmium and lead ions the surface of pyrophyllite showed flat crystals, book like structure, and smaller amounts of fibrous phase as shown as in Figs. 12(a) and 13(a), respectively. The figures show the changes in morphological features after treatment with metal ions.

The EDX spectrum for bulk sample and the mapping of different constituent elements indicates the presence of Na, K, Al, Si, and O (Fig. 11(b)). The figure is the general view of the sample showing wide size range of the particles. The studies showed that potassium is embedded in the sample in the form of minute particulate matter and are not present uniformly. It is associated with very trace levels and is adsorbed or embedded within these elemental phases. The EDX spectrum of pyrophyllite after adsorption with cadmium ions (Fig. 12(b)) gives the characteristic peaks for cadmium at 2.95 keV indicating the adsorption of cadmium ion in the pyrophyllite surface.

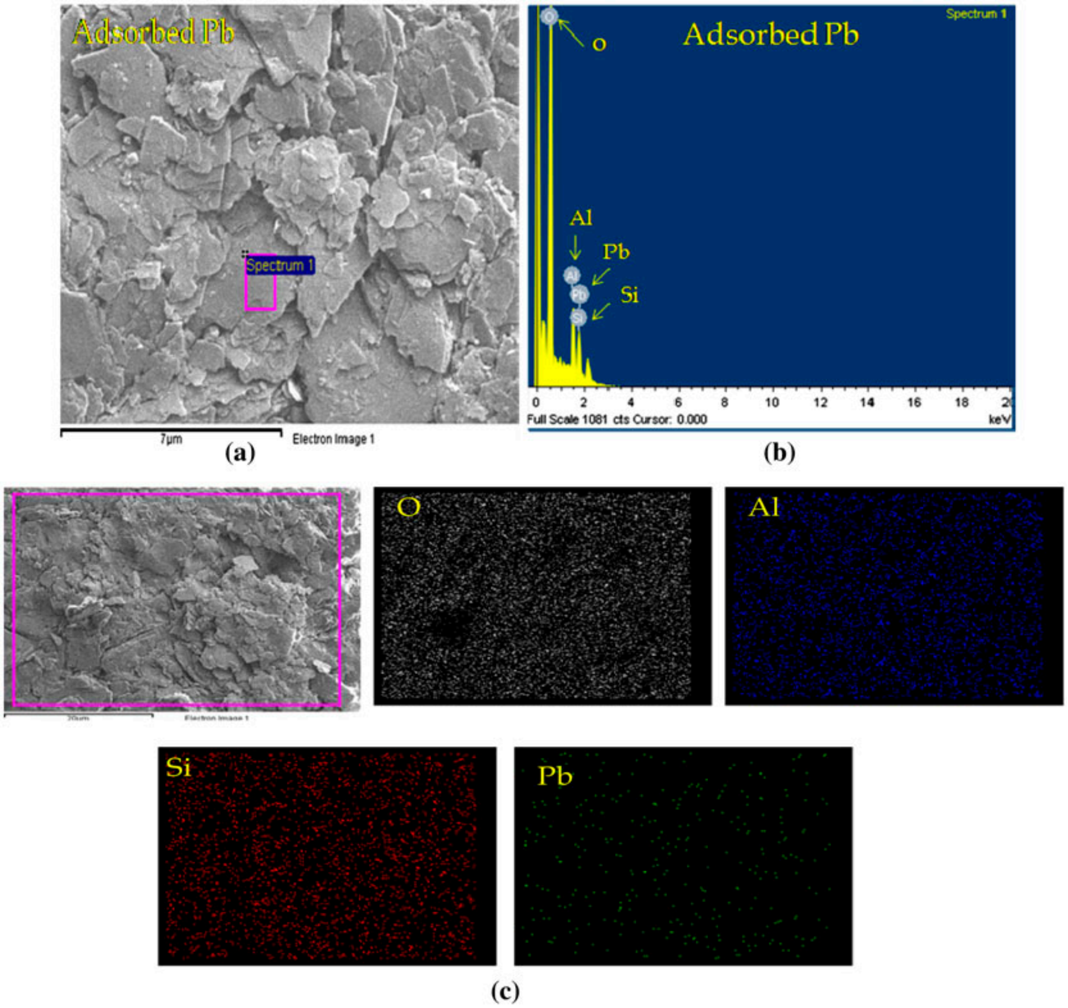

Fig. 13. (a) FESEM-EDX micrographs for lead-adsorbed surface of pyrophyllite and (b) EDX (c) mapping of constituent elements Si, O, Al, and Pb in adsorbed sample.

Similarly, the characteristic for Pb ion is seen in 1.97 keV (Fig. 13(b)). The electronic mapping of the bulk sample indicates the presence of O, Al, Na, and K ions (Fig. 11(c)). The rectangle shows the analyzed region for different ions. The cadmium ions adsorbed on pyrophyllite surface is clearly visible indicating its presence in the whole edges of the material (Fig. 12(c)). In the case of lead ions, the image reveals that most of the lead ions onto loaded surface of pyrophyllite are homogeneously distributed on the surface (Fig. 13(c)). The EDX spectrum of pyrophyllite after adsorption of lead ions (Fig. 13(b)) gives the characteristic peaks for lead at 2.95 keV indicating the adsorption of this ion in the pyrophyllite surface.

Considering the adsorption capacity of pyrophyllite with lead and cadmium ions, the possible mechanism of adsorption with pyrophyllite is shown below.

$$\mathrm{Cd}^{2+} + 2(\mathrm{Al{,}SiO})^{-}\mathrm{K}^{+} \leftrightarrow (\mathrm{Al\ SiO})_2\mathrm{Cd} + 2\mathrm{K}^{+} \tag{10}$$

$$\mathrm{Pb}^{2+} + 2(\mathrm{Al{,}SiO})^{-}\mathrm{K}^{+} \leftrightarrow (\mathrm{Al\ SiO})_2\mathrm{Pb} + 2\mathrm{K}^{+} \tag{11}$$

4.3. XPS study

The X-ray photoelectron spectroscopy (XPS) spectra of bulk pyrophyllite waste sample and pyrophyllite adsorbed with cadmium and lead ions were analyzed and shown in Fig. 14. In pyrophyllite spectra, the peak around 72.9 and 100.2 eV corresponds to Al (2p) and Si (0), respectively. The peak of 531.8 eV corresponds to O (1s) [34]. The spectra of pyrophyllite sample adsorbed with cadmium has indicated a small peak at 408.0 eV corresponds to Cd (3d) which is

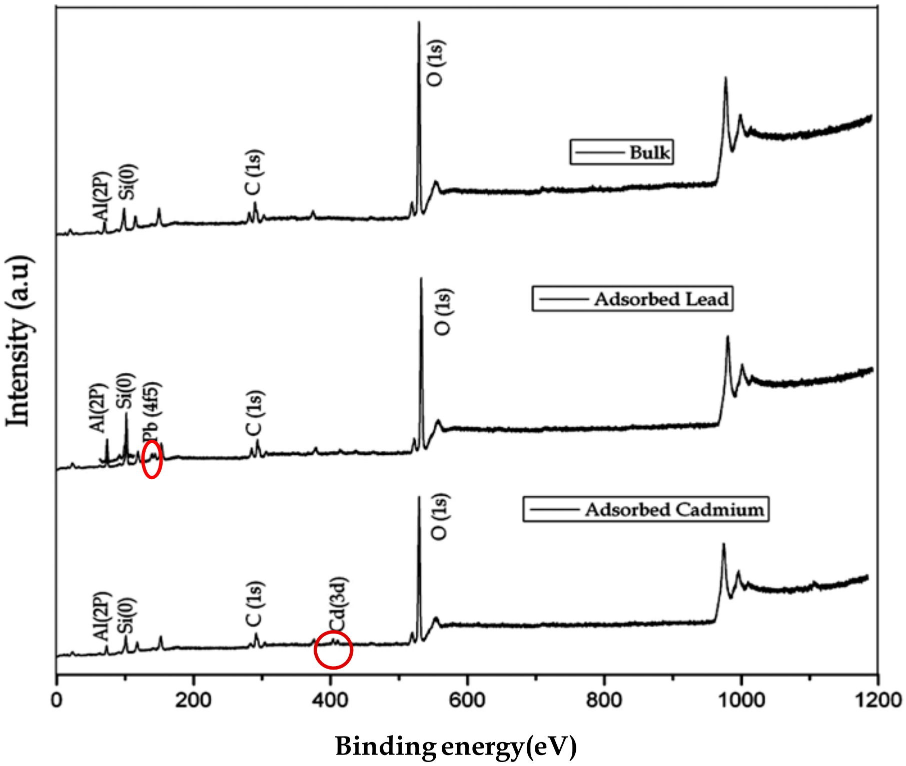

Fig. 14. XPS spectra of pyrophyllite and pyrophyllite adsorbed with cadmium and lead.

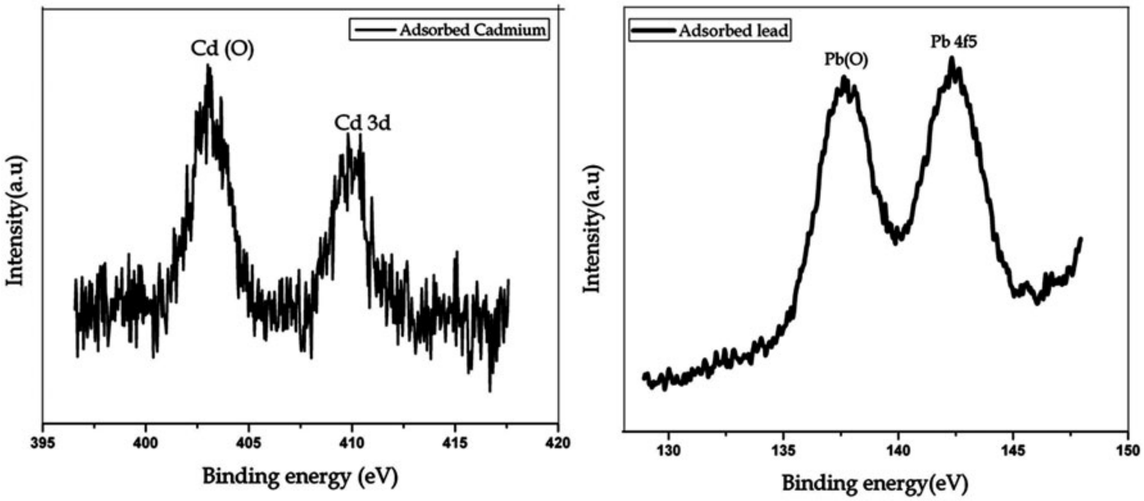

Fig. 15. XPS spectra of adsorbed cadmium and lead.

absent in the pyrophyllite spectra. Similarly, the new peak at 141.7 eV observed in the case of pyrophyllite loaded with lead ions corresponds to Pb (4f), which shows the presence of lead ions and confirms the adsorption onto the pyrophyllite waste surface. Fig. 15 represents the broad region of spectra of adsorbed cadmium and lead in pyrophyllite waste sample that clearly confirms the presence of cadmium and lead adsorption on to the pyrophyllite surface. In all cases, the unchanged peaks of Si (0) and Al (2p) indicate there was no adsorption on those surfaces and remains unaltered [35].

Table 1
Comparison of adsorption capacities of various adsorbents for lead and cadmium metal ions

Pb^{2+} adsorption			Cd^{2+} adsorption		
Adsorbent	q_{max} (mg/g)	Ref.	Adsorbent	q_{max} (mg/g)	Ref.
Blast furnace slag	40	[36]	Palygorskite	4.54	[42]
Activated carbon	30	[37]	Perlite	0.64	[43]
Kaolinite clay	4.5	[38]	Dolochar	1.9	[12]
Talc	8.0	[39]	Montmorillonite	6.3	[44]
NALCO plant sand	22.8	[40]	Bentonite	11.2	[44]
Red mud	6.02	[41]	Kaolinite clay	4.38	[38]
Pyrophyllite mine waste	43.47	Present work	Pyrophyllite mine waste	4.58	Present work

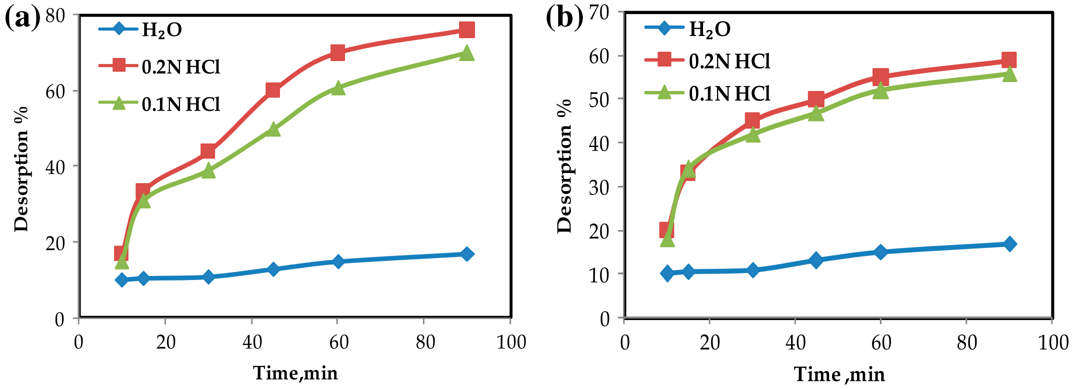

Fig. 16. Desorption study of cadmium (a) and lead (b).

Finally, the adsorption capacity of pyrophyllite waste for both Cd(II) and Pb(II) was compared with the reported values [36–42] for waste materials and are shown in Table 1. From the results, it is evident that waste material from pyrophyllite mines is comparable to many adsorbents for treating wastewater containing Pb(II) and Cd(II) metal ions.

5. Desorption study of cadmium and lead ions

It is not applicable to discard Cd(II)- and Pb(II)-loaded pyrophyllite samples into the environment. These pollutants will slowly release into the surrounding environment leading to the contamination of soil and water systems. It is required to desorb both the metal ions from the adsorbent by a cheaper desorption method. Desorption study of loaded pyrophyllite can also be reused for another cycle of adsorption. It was found from the effect of pH studies that slightly higher adsorption of both the metal ions takes place at alkaline pH values. As a result, desorption of metal ions was carried out at acidic pH only. The removal of cadmium and lead ions were performed after treatment with two different concentrations of HCl and represented in Fig. 16. The studies were also compared with distilled water at various time of agitation. It was observed that the maximum desorption achieved for lead and cadmium ions are 59 and 76%, respectively, by using 0.2 N HCl solution. The distilled water agitation has negligible impact on desorption study.

6. Conclusion

In this investigation, the ability of pyrophyllite waste as a natural adsorbent to remove cadmium and lead ion from aqueous solution was studied. Experimental values show that pyrophyllite waste can be used as an effective adsorbent for the removal of these ions from aqueous solution. The adsorbent used in this study is natural and freely available. Results obtained were modeled by using two isotherm models such as Langmuir and Freundlich. Equilibrium isotherms were well described by the Langmuir equation, giving maximum adsorption capacity of 43.47 mg/g at 300 K for lead and 4.58 mg/g for cadmium. The pseudo-second-order equation well fits the adsorption kinetics. The positive value of enthalpy indicates that the adsorption process is endothermic in nature. Thus, the pyrophyllite waste can be used as an effective adsorbent for the removal of cadmium and lead ions from aqueous solutions.

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