Original research

Adsorption of Heavy Metals on Chemically Modified Muscovite

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Abstract:

Effective adsorbent was prepared from Egyptian Muscovite by activation with H_2O_2, HCl and/or H_2O_2 / HCl. The prepared adsorbents were applied for the removal of cadmium and lead from polluted water. Raw Muscovite powder was activated by different treatments using 30% H_2O_2, HCl, and/or HCl /H_2O_2. Optimum adsorption conditions of pH, adsorbent dose, initial metal concentration, stirring time and solution temperature were optimized for the maximum adsorption of Cd and Pb. The results reveal that the Muscovite adsorbent prepared with a mixture of HCl /H_2O_2 shows the higher adsorption of Cd and Pb than that with HCl or H_2O_2. The maximum adsorption of Cd and Pb by the developed adsorbent was 97.8% and 98.1%, respectively at 60 min ,25°C, initial metal concentration 50 ppm, adsorbent dose 2g/50 mL solution and pH 6 for lead and pH7 for cadmium. Adsorption isotherms and kinetic models were investigated and ended to that the adsorption of Pb and Cd fitted well Langmuir adsorption isotherm.

Keywords: adsorption, Muscovite, acid activation, purification, heavy metals

1- INTRODUCTION

Water pollution is one of the most serious environmental problems which is caused by a variety of human activities such as industrial, agricultural and domestic.

High concentration of heavy metals and other inorganic pollutants contaminate the water. Heavy metals are becoming more prominent due to the diverse routes of its exposure, its toxic implications across time scales and the level of industrial development in recent decades. The presence of heavy metal ions (e.g. Hg, Cu, Cd, Pb, As, and Se) in water, even at very low levels, can cause damage to ecosystem and human life, because they are not biodegradable (Badawy et al., 2010; El-Bayaa et al., 2009).

Lead and cadmium are two common toxic heavy metals that man is increasingly being exposed to due to their properties and wide applications in materials and technologies that define human survival.

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High concentrations of lead is known to cause encephalopathy, cognitive impairment, kidney and liver damage, anemia and toxicity to the reproductive system (Pagliuca and Mufti, 1990; O'Connell et al.,2008; Adekunle et al., 2014).

Methods used to remove heavy metals from polluted water and wastewater include, coagulation reduction, precipitation and flotation, adsorption, ion exchange, membrane technology, electrochemical treatment, electrolysis, and membrane processes, and adsorption (Yang et al., 2010 ; Mahdavi et al., 2013). Among these technologies, adsorption has the additional advantages of applicability at very low concentrations. Natural materials such as chitosan, zeolites, clays, or certain waste products from industrial operations (such as fly ash, coal, and oxides) are classified as low-cost adsorbents compared to activated carbon (Cheira et al.,2019a,b; Shawky et al.2019; Rashed et al.2017, 2018,2019).

Clay refers to a class of materials generally made up of layered silicates or clay minerals with traces of metal oxides and organic matter. Clay minerals are widespread and abundant in aquatic and terrestrial environments and, being finely divided, have large surface areas per unit of mass (Abollino et al., 2008). Muscovite is a hydrated magnesium aluminum silicate mineral formed by weathering biotite and iron-bearing phlogopite micas. It has several advantages such as high availability, easy handling, low-cost adsorbent, and selectivity over other natural adsorbents (Katsou et al., 2011). Muscovite $KAl_2[Si_3AlO_{10}(OH)_2]$ is one of clay mineral which belongs to mica group while quartz can be present in clay materials in lower proportion. The minerals of the mica group consist of layers of one octahedral $Al(O/OH)_6$-sheet sandwiched by two tetrahedral SiO_4-sheets (Muazu et al.2020)

Schmidt et al. (2012) studied adsorption of tetravalent thorium to the (0 0 1) basal surface of the phyllosilicate muscovite from an aqueous solution, and found that the uptake measurements of the adsorption to the Muscovite surface follows a Langmuir isotherm. Yang et al. (2010) reported adsorption of As (III), As(V), Cd (II), Cu (II), and Pb (II) from aqueous solutions by natural Muscovite (NM), and found that the adsorption of the metals was greatly influenced by solution pH but not by ionic strength. The maximum adsorption capacities of NM were 0.791, 0.750, 0.630, 0.618, and 0.330 mg g−1 for As(V), Cd (II), Pb (II), Cu (II), and As (III), respectively. Although NM is cheaper than purified muscovite, the adsorption capacities of NM are less than those of purified materials. Hamidpour et al. (2019) studied adsorption of cadmium and zinc onto Micaceous minerals (muscovite and phlogopite) the effect of hydroxamate siderophore deferoxamine B (DFOB) on cadmium (Cd) and zinc (Zn) adsorption, and reported that the presence of DFOB diminished the adsorption of Cd and Zn onto both minerals, particularly under neutral to alkaline pH conditions.

This study aims to prepare an effective adsorbents from Muscovite by chemical activation with H_2O_2, HCl and/or H_2O_2 / HCl, and appleing the resulted adsporbents for the removal of Pb and Cd from its solution.

2- MATERIALS AND METHODS

2.1. Chemicals and Reagents
Standard stock solutions of 1000 ppm Pb and Cd ions were prepared by dissolving appropriate amounts of analytical grade reagent [cadmium nitrate tetrahydrate-Cd $(NO_3)_2.4H_2O$ (Sigma-Aldrich) (99% assay) and $Pb(NO_3)_2$ (Sigma- Aldrich) (99% assay)] in deionized water using a 1000 mL volumetric flask (MBL Boro England). The stock solutions were acidified to prevent hydrolysis by adding 5 mL HNO_3 and the volume was made up to the 1000 mL.

2.2. Characterization of activated Muscovite adsorbent

Morphology of Muscovite and activated Muscovite adsorbent was examined using SEM, XRD and FTIR. Micromeritics Tristar 3000 (Georgia, USA) instrument, utilizing $N_2(g)$ adsorption technique, was used to determine the surface area and porosity of Muscovite and activated Muscovite adsorbent samples.

2.3. Sample collection

Muscovite mineral supplied from Elhafafet area (south of east desert, Egypt) was used as raw material in this study. Muscovite samples had dark gray color. Five bulk samples (5kg) were collected from the area. The samples were crushed and ground to powder with a laboratory agate mortar. The silica particles were removed from muscovite samples by contact the powdered muscovite with deionized water for one day, filtered, dried at $60^{o}c$ for 24h and, sieved to 565 μm. The chemical composition of Muscovite sample was detected by XRF as shown in Table 1. Table 1.

Table (1) Chemical composition of raw Muscovite sample.

SiO_2%	Na_2O%	K_2O%	Al_2O_3%	Cd ppm	Zn ppm	Pb ppm	Cu ppm
48.16	0.72	10.62	32.5	12.70	0.482	UD	UD

2.4. Preparation of Muscovite adsorbents

2.4.1 Purification of Muscovite

10g Muscovite was placed in 100 mL ultrapure water and sonicated for 10 min, let the solution stand down for 10 min and after then separated by decantation. Repeated this step twice, filtered the solution and dried in 60°C for 24h (Sis and Uysal,2014).

2.4.2. Chemical activation of Muscovite

2.4.2.1. Activation with hydrochloric acid
Activation of the muscovite was run by mixing of the purified powder muscovite with different HCl concentration at different times.

5 gm purified muscovite was mixed with 200 mL HCl (concentration 0.5, 0.8, 1.5 and 2 M), stirred at $25^{o}C$ for 8, 10 and 12 hr, filtered, washed with deionized water till the solution became neutral (the filtrate was tested with $AgNO_3$) and dried at $100^{o}C$ for 10 hours. All the developed adsorbents were grounded in an agate mortar and sieved to 63μm (Hashem et al, 2015). The developed activated Muscovite adsorbents were labeled (AM1-AM12)

2.4.2.2. Activation with hydrogen peroxide H_2O_2 (30%)

Chemical activation of Muscovite with H_2O_2 was done by treatment with 30% H_2O_2 solution. 5 g of purified Muscovite was stirred with 200 mL 30% H_2O_2 for 6 ,7 and 8h, filtered, washed several times with deionized water, and dried in oven at 100 °C for 24h (Hashem et al, 2015). All the developed adsorbents were ground in an agate mortar and sieved to 63μm (AM13-AM15).

2.4.2.3 Activation with mixture of hydrochloric acid and hydrogen peroxide
2.4.2.3.1. HCl/ H_2O_2 (vol / vol)
5 g of purified muscovite was mixed with 200 mL 0.8M HCl, stirred at $25^{o}C$ for 10 hr, filtered, washed with deionized water till the solution became neutral (the filtrate was tested with $AgNO_3$) and dried at $100^{o}C$ for 10 hr. Then 5g of acid activated muscovite (from the previous step) was

mixed in 200 mL 30% H_2O_2, stirred mechanically for 7 hr, filtered, washed with deionized water till the solution became neutral and dried at 100^oC for 10 hr. The developed adsorbent was grounded in an agate mortar and sieved to 63μm. The developed activated muscovite adsorbent was labeled (AM16).

2.4.2.3.2. HCl/ H_2O_2 (wt by wt)

2.5g of activated muscovite by 0.8M HCl for 10h and 2.5 g of activated muscovite by H_2O_2 (30%) for 7 hr was mixed mechanically in an agate mortar, and sieved to 63μm. The developed activated muscovite adsorbent was labeled (AM17)

2.4.3. Selection of the best adsorbent

For selecting the best adsorbent for the removal of Pb and Cd from its solution, the following experiments were applied

2.4.3.1. Adsorption of cadmium and lead

0.2 g of each of the prepared activated muscovite samples (AM1- AM17) was stirred with 50 mL of 50 ppm Cd^{2+} and Pb^{2+} for 2 hr and pH solution was adjusted at pH 6 using HNO_3 or NaOH solution. The mixture was then filtered and the metal ions in the filtrate were measured by atomic absorption spectrophotometer.

2.4.6. Batch adsorption experiments

Batch mode experiments were done for the removal of both Cd^{2+} and Pb^{2+} ions on raw and chemically activated Muscovites. Batch adsorption experiments examined the effect of solution pH, initial of adsobate concentration, solution temperature, adsorbent dosage, and contact time.

2.3.6.1. Effect of pH

Adsorption experimenters for the effect of solution pH on metal adsorption were conducted as follows: 0.5 g of the activated muscovite was stirred with 50 mL of 50 ppm standard solution of single ions Cd^{2+} and Pb^{2+} for 2hr. Solution pH was adjusted at 2, 4,5, 6,7,8 and 10 using HNO_3 or NaOH solution. The mixture was then filtered and the metal ions in the filtrate were measured by atomic absorption spectrophotometer

2.3.6.2. Effect of adsorbent dosage

Different amounts (0.5, 1.0,1.5 and 2.0 g) of activated muscovite was stirred with 50 mL of 50 ppm standard solutions of single ions for 2hr and adjusted the pH at 6 for Pb^{2+} and 7 for $Cd^{2+.}$ The mixture was filtered and the metal ions in the filtrate was measured by atomic absorption spectrophotometer

2.3.6.3. Effect of initial concentration of heavy metals

2.0 g of activated muscovite was stirred with 50 mL of a metal standard solution (Cd^{2+} and Pb^{2+}) for 2hr at pH 6 for Pb^{2+} and pH 7 for $Cd^{2+.}$, at different metal concentration (10,20,30, 50, 75 and 100 ppm) as initial concentration. The temperature was constant at 25ºC. The mixture filtered and the metal ions in the filtrate were measured by atomic absorption spectrophotometer.

2.3.6.4. Effect of contact time

2.0 g of activated muscovite was stirred with 50 ml of 50 ppm of both Cd^{2+} and Pb^{2+} at pH 7 for Cd^{2+} and pH 6 for Pb^{2+}. The effect of contact time was investigated for 30, 60, 120 and 180 min

with solution temperature at 25ºC. The mixture was filtered and the metal ions were measured by atomic absorption spectrophotometer.

2.3.6.5. Effect of temperature

On stabilizing all above mentioned parameters. The effect of adsorption temperature was investigated at temperatures 25, 35, 45 and 55ºC. The solution was filtered and the metal ion concentration (Cd^{2+} and Pb^{2+}) in the filtrate was measured by atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Muscovite before and after purification

3.1.1. SEM examination

SEM micrographs of raw and purified muscovite (Figs.1-2) showed appearance of separated particles that particles are plate-like and the aggregated plates are compact from the edges with the face dimension of most particles being less than500 μm. The muscovite layers are closely stacked together due to strong intermolecular forces (Fig. 1). After purification, the muscovite samples had a black grey appearance with increase in the surface undulation and in the interlayer thickness with no change in the particle basal dimensions. The internal layer space became less than 63 μm (Fig. 2).

3.1.2. XRD analysis

For determination the structural change of muscovite before(BP) and after(AP) purification using XRD diffraction patterns was shown in Fig (3), the XRD of muscovite adsorbent before purification confirmed the presence of Muscovite (80)%, Glauconite(12%) Jahnsite(5%), and Zinnwaldite(3%)(Sander et al.2020) .After purification, it exhibited Muscovite(90%), Coesite(3%) and Richterite(7%).From Fig (3), high intensity of Muscovite peaks at $2\theta =$ (9.7,27.1 and 35.98º) while lower intensity of peak at $2\theta = $ (18, 37.2 and 45.43º). Ismail et al,2017 found that the d(002) (9.9 Å) of the main peak indicates that the original sample is muscovite.
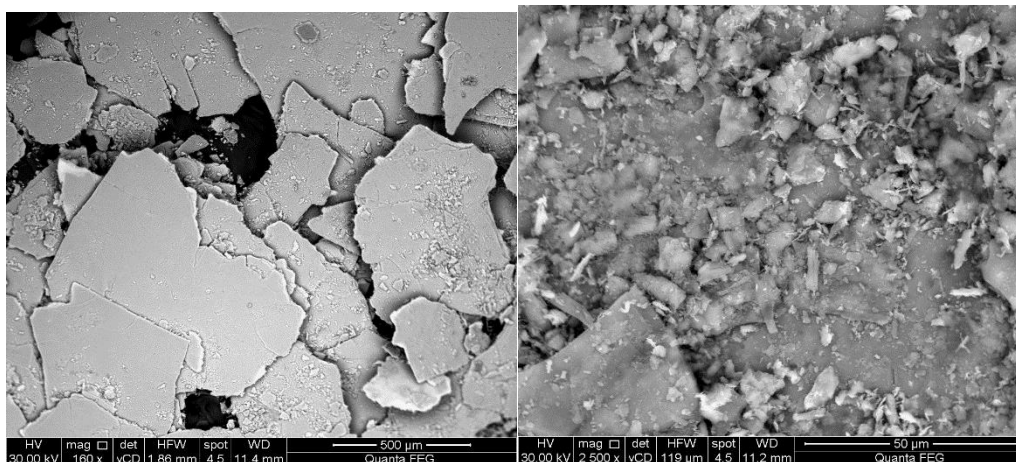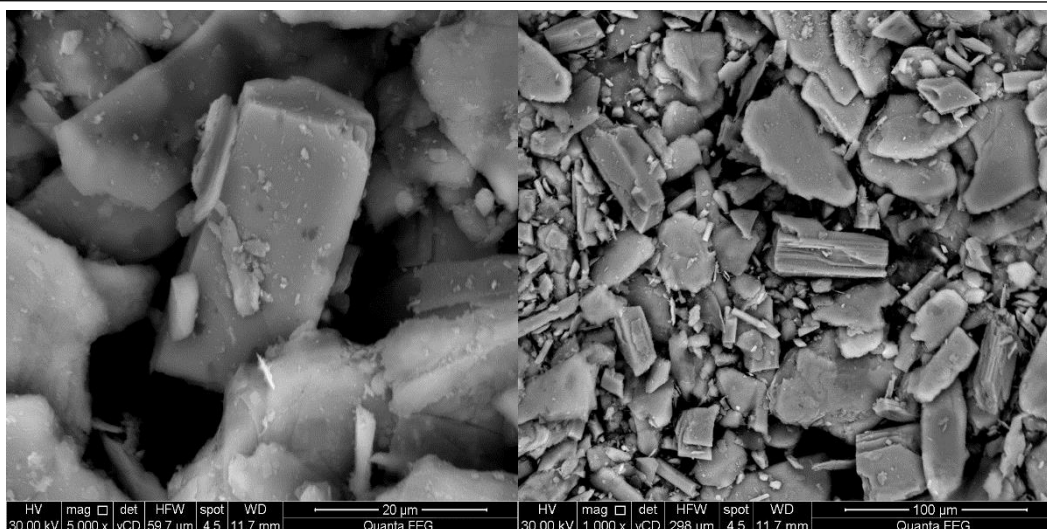

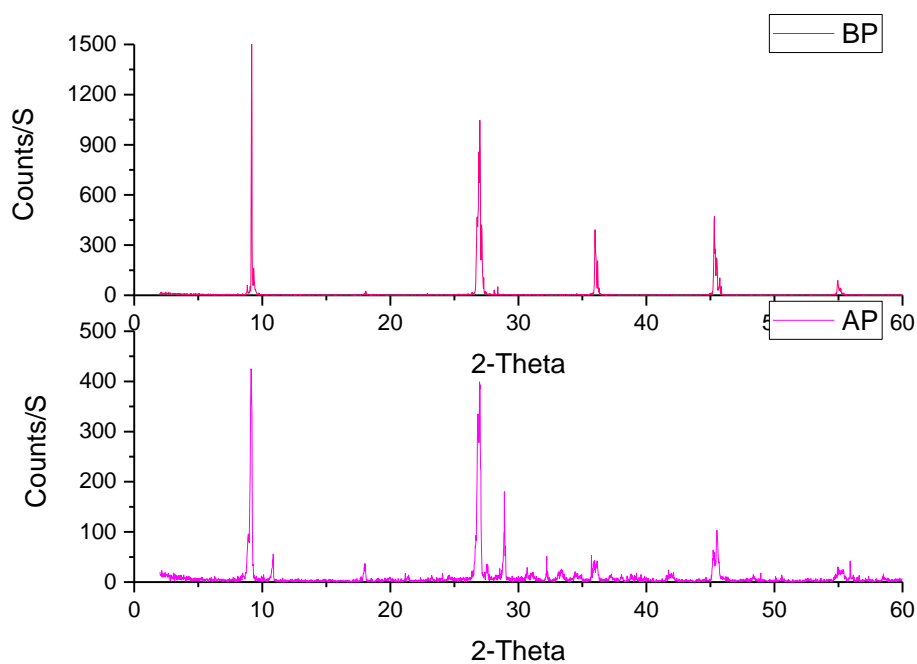Fig. 1. SEM of raw Muscovite

Fig. 2. SEM of purified muscovite

Fig. 3. XRD of raw and purified muscovite

3.1.3. FTIR analysis

FTIR spectroscopy is an effective analytical instrument for detecting functional groups and characterizing the covalent bonding information. As shown in Fig. (4), the FTIR spectra reveal the structural differences between raw and purified muscovite.

The absorption band at 3624 cm is due to the OH stretching vibration. Based on the transmittance bands, the structure of raw muscovite is similar with purified muscovite. The peak at 1113 cm^{-1} is assigned to Si-O stretching (longitudinal mode), while 1024–1019 cm^{-1} is the in-plane Si-O stretching
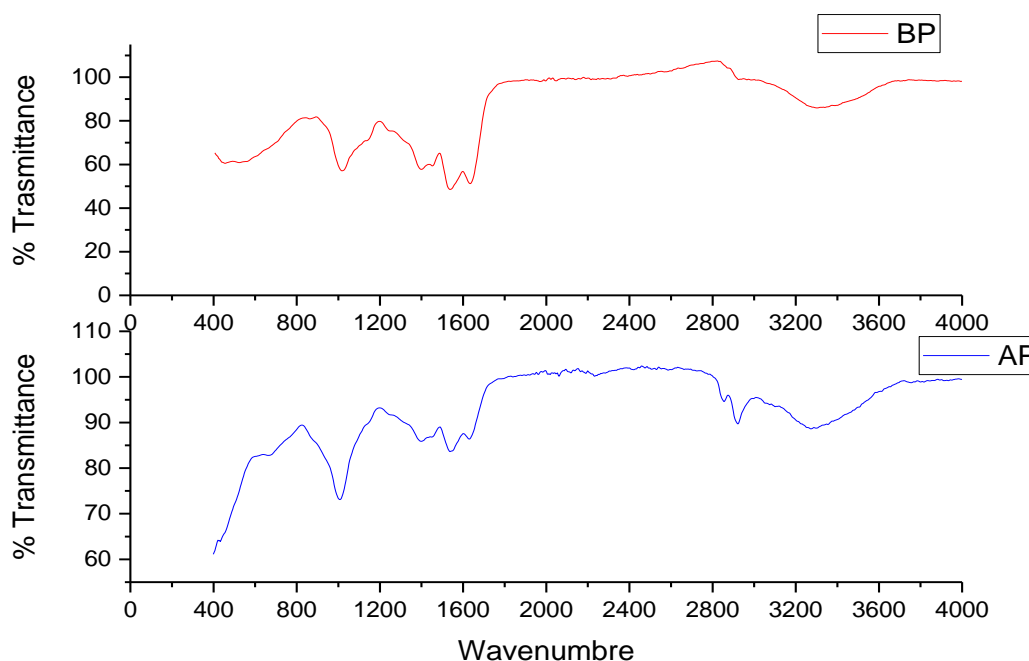
Fig.4 FTIR of raw and purified muscovite

3.1.4. Surface area, BET and BJH analysis

The surface area of samples was estimated by the BET method (Table 2). It was found that the surface area values for raw Muscovite was 55.97 m^2/g, while that for purified Muscovite it was 80.526 m^2/g. These results indicate the increase of the surface area of the purified Muscovite than that of the corresponding raw.

The pore size distribution was obtained by application of the BJH (Barrett-Joyner-Halenda) method for the desorption isotherm of the samples. Table (2) shows that the pore size of raw Muscovite was 16.14 nm, and that for purified was 15.537 nm.

The pore size of purified was smaller than the pore size of raw due to decreasing the particles of Muscovite via grinding.

Table 2. The pore size and surface area of raw and purified Muscovite

Sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Raw Muscovite	55.97	16.14	0.04184
Purified Muscovite	80.5266	15.537	0.097

3.2. Characterization of Activated Muscovite

3.2.1. XRD analysis

For determination the structural changes of the developed Muscovite before (PM) and after(AP) activation using XRD diffraction patterns of adsorbent was shown in Fig (5), the XRD of muscovite adsorbent before activation confirmed the presence of Muscovite, Coesite and Richterite. After activation it exhibited Illite, Biotite, Ankerite and Hematite, Quartz and

Fluorophlogopite. Illite detected after activation, because muscovite may be transformed to illite by chemical processes. From Figure (5), high intensity of peaks at 2θ = (8.94 & 26.56°) while lower intensity of peak at 2θ = (17.8, 35.9 and 45.32°) for illite was observed. Biotite has low intensity peak at 2θ = (34.2, 37.1, and 55.1°). Moreover, it was noticed that peaks at 2θ = (30.9, 33.1, 37.1 and 55.1°) refer to the presence of Ankerite, 2θ = (33.1, 35.9, 37.1 and 55.1°) for Hematite, 2θ = (17.1, 20.8 and 55.1°) for Quartz and Fluorophlogopite shows low intensity peak at 2θ = (17.8, 24.5, 30.9, 33.1, 34.2 and 41.8°).
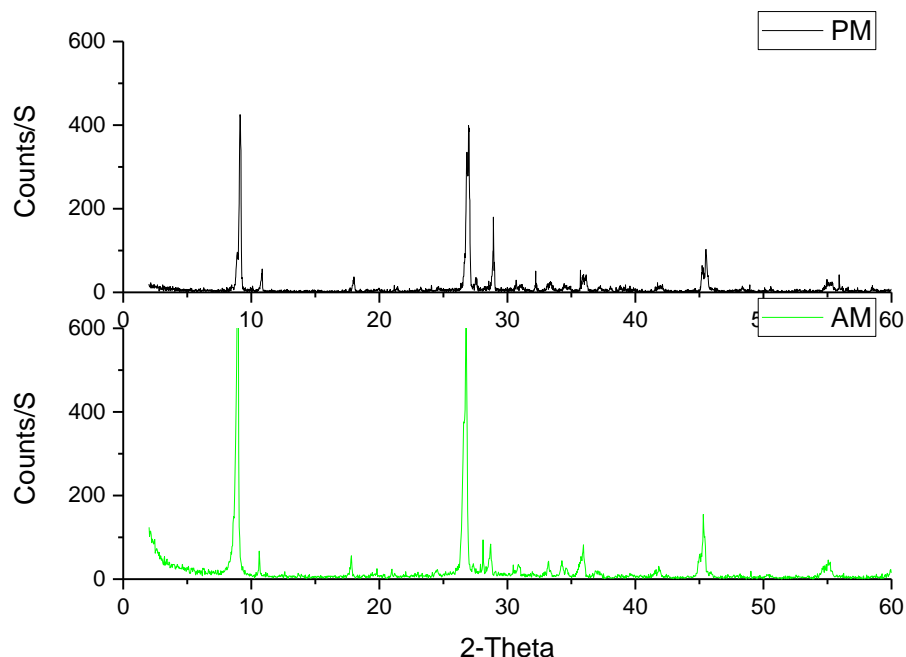

Fig. 5. XRD of purified and activated muscovite

3.2.2. FTIR analysis

As shown in Fig. (6), the FTIR spectra reveal the structural differences between purified and activated muscovite. The absorption band at 3624 cm was no longer exist due to illite formation. The peak at 1113 cm^{-1} is assigned to Si-O stretching (longitudinal mode), while 1024–1019 cm^{-1} is the in-plane Si-O stretching.

3.2.3. Surface area, BET and BJH analysis

The surface area of samples was estimated by the BET method (Table 3). It was found that the surface area values for purified Muscovite was 80.5266 m^2/g, while that for activated Muscovite it was 137.659 m^2/g. These results indicate the increase of the surface area of the activated Muscovite than that of the corresponding purified.

Table 3. The pore size and surface area of purified and activated Muscovite

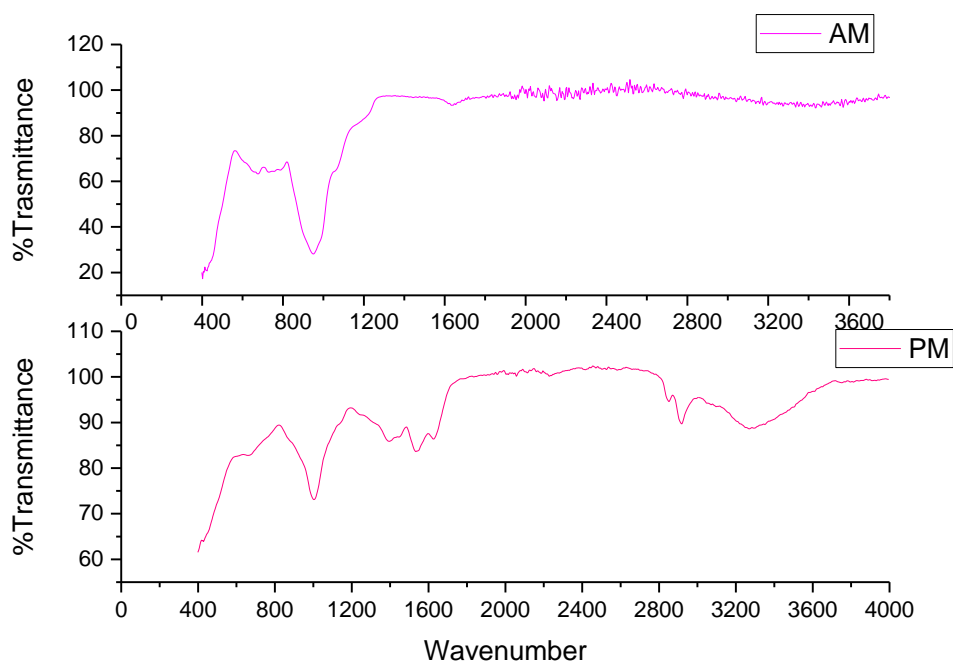| Sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Purified Muscovite	80.5266	15.537	0.097
Activated Muscovite	137.659	14.501	0.145

Fig. 6. FTIR of purified and activated muscovite

3.3. A comparative study of the developed activated Muscovite for lead and cadmium removal efficiency

The chemical activation of muscovite (Table4,5 and 6) showed that for the activation of muscovite with hydrochloric acid , the removal percent of Pb was the best at 0.8M hydrochloric acid (87%) at stirring time 10h(AM5) and (85.4%) for H_2O_2 (30%) (AM14) at stirring time 8h and also the removal percent of Cd was the best at 0.8M hydrochloric acid (67%) at stirring time 10h and (67.6%) for H_2O_2 (30%) at stirring time 8h. So, the developed adsorbents AM5 and AM14 were selected as the most chemically activated Muscovite adsorbents

Table (4). Removal percent of lead and cadmium by chemically activated Muscovite adsorbent with HCl .

	Pb			Cd		
Stirring time	8h	10h	12h	8h	10h	12h
HCl Conc. (M)	% removal	% removal	% removal	% removal	% removal	% removal
0.5	67.7	71.7	73	55.9	63.3	61.2
0.8	84.4	87	76.8	65.8	67	62.9
1.5	72.5	78.5	75.8	63.8	64.2	62
2	75	75.4	71	62.7	64	61.7

Table (5). Removal percent of lead and cadmium by chemically activated Muscovite adsorbents with $H_2O_2(30\%)$

Stirring time (h)	Pb	Cd
	Removal %	Removal%
6h	74.9	57.8
7h	85.4	67.9
8h	78.7	60.6

Table 6. Removal percent of cadmium and lead by chemically activated Muscovite adsorbents with $H_2O_2(30\%)$ and HCl

Stirring time (h)	Removal % Pb	Removal % Cd
H_2O_2+HCl (AM16)	85.9016	81.7792
H_2O_2+HCl (AM17)	94.9576	83.6572

3.4. Optimum parameters for the adsorption of heavy metals on activated Muscovite

3.4.1. Effect of pH on heavy metals adsorption

The pH of Cd^{2+} and Pb^{2+} solution plays an important role in the whole adsorption process. The effect of solution pH on the adsorption of Cd^{2+} and Pb^{2+} on activated Muscovite were determined at pH 2,4 5,6 7,8 and 10 with fixed adsorbent dose of 0.2 g /50 ml, heavy metals concentrations 50 ppm, temperature 25^oC and contact time 120 min. The pH of the solution was controlled by addition of 0.1 M HNO_3 or 0.1 NaOH. The results showed in Figure (7) pointed that the removal percentage of Cd^{2+} and Pb^{2+} increased with increased pH from 2 to 7 for Cd^{2+} and from 2 to 6 for Pb^{2+}. Adsorption removal percentage increased for Cd^{2+} from 20.4 to 64.6 %, for Pb^{2+} from 39.2 to 72.8%.

At low pH (less than 4.0) heavy metal removal was inhibited, possibly as a result of a positive charge density on metal binding sites due to a high concentration of protons in solution. With an increase in the pH, the negative charge density on the activated carbon surface increases due to deprotonation of the metal binding sites and thus increases adsorption. Experiments were carried out with the pH values of 7 due to the fact that metal precipitation appeared at higher pH values (Puranik et al, 1997; Gadd,1988)

3.4.2. Effect of adsorbent dosage

In these experiments, Cd^{2+} and Pb^{2+} solutions with a concentration of 50 ppm were placed in contact with various amount of activated Muscovite (0.1,0.2,0.3,0.5,1.0,2.0 and 3.0 g), keeping other parameter (pH, contact time and temperature) constant.

The results are presented in Figure (8) show that the removal percentage of Cd^{2+} and Pb^{2+}increases with increase activated muscovite adsorbent dose. The removal percentage of Cd^{2+} increase from 42.8 % to 96.7% and from 58.4% to 97.6% with increase in adsorbent dose to 2g. This increase of heavy metals removal resulted from the increase of the number available adsorption site in adsorbents till certain number after that accumulation on adsorbent occurred, so

removal percentage decrease. With increasing adsorbent dosage more surface area is available for the adsorption due to increase in active sites on the adsorbent and that increasing this number had also no effect after equilibrium was reached (Gerçel and Gerçel,2007).
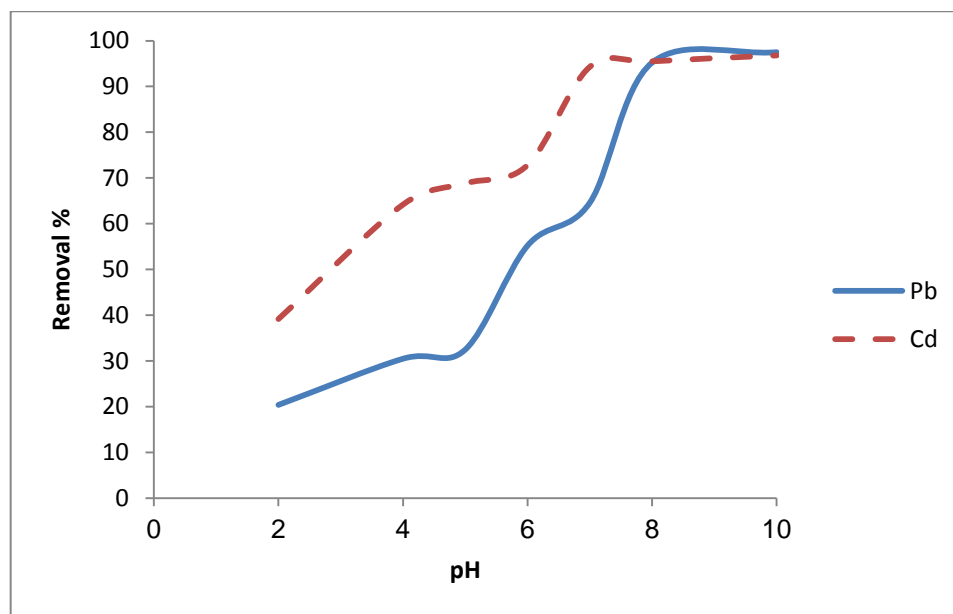

Fig7. Adsorption of Cd^{2+} and Pb^{2} on activated muscovite according to pH
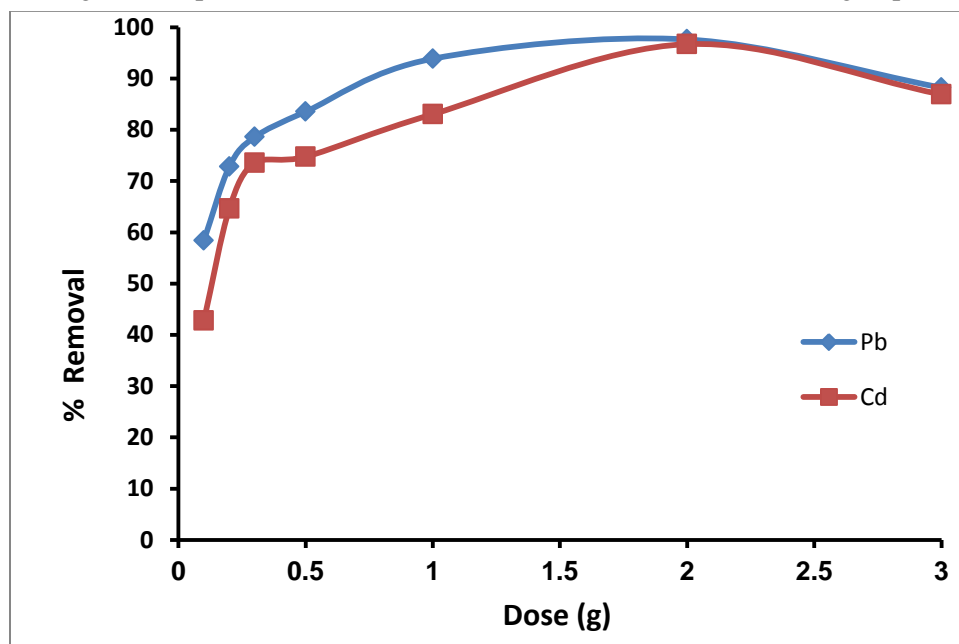

Fig. 8. Adsorption of Cd^{2+} and Pb^{2+} on activated muscovite according to adsorbent dose

3.4.3. Effect of initial heavy metals concentration on the adsorption

The optimum Cd^{2+} and Pb^{2+} initial concentration for the maximum adsorption on activated Muscovite adsorbent was studied by varying the Cd^{2+} and Pb^{2+} concentration from 10-100 ppm, at constant temperature 25°C, adsorbent dose 2.0 g, pH 7 for Cd^{2+} and pH 6 for Pb^{2+} contact time at 120 min. The effect of initial concentration on the removal of Cd^{2+} and Pb^{2+} by the adsorbent

was represented in Figure (9). The data evident that removal percentage increases from 68.52%, 70.7% to 96.7%, 97.6%, then decreases to 72.8%, 85.23% for Cd^{2+} and Pb^{2+} respectively with increase concentration. This is due to that with increase concentration, surface area and active sites of the adsorbent saturated and hence percentage removal decreases. This result refers to that the best concentration of Cd^{2+} and Pb^{2+} was 50 ppm for the adsorption on activated Muscovite adsorbent. At low metal concentrations, the ratio between the active sites and metal ions was high which favor the adsorption of the heavy metal ions and hence the removal efficiency increased. Concentration increasing of metal ions would lead to decreasing in the diffusion velocity of the heavy metal ions (Erdem et al., 2004). Besides, it allows each active site to be subjected to a larger number of metal cations that decreases the driving force for the removal process which, by its role, decreases the overall removal efficiency. Similar result was found by Wu et al. (2008) who reported that the increase of initial zinc concentration leads to a reduction of the removal efficiency.
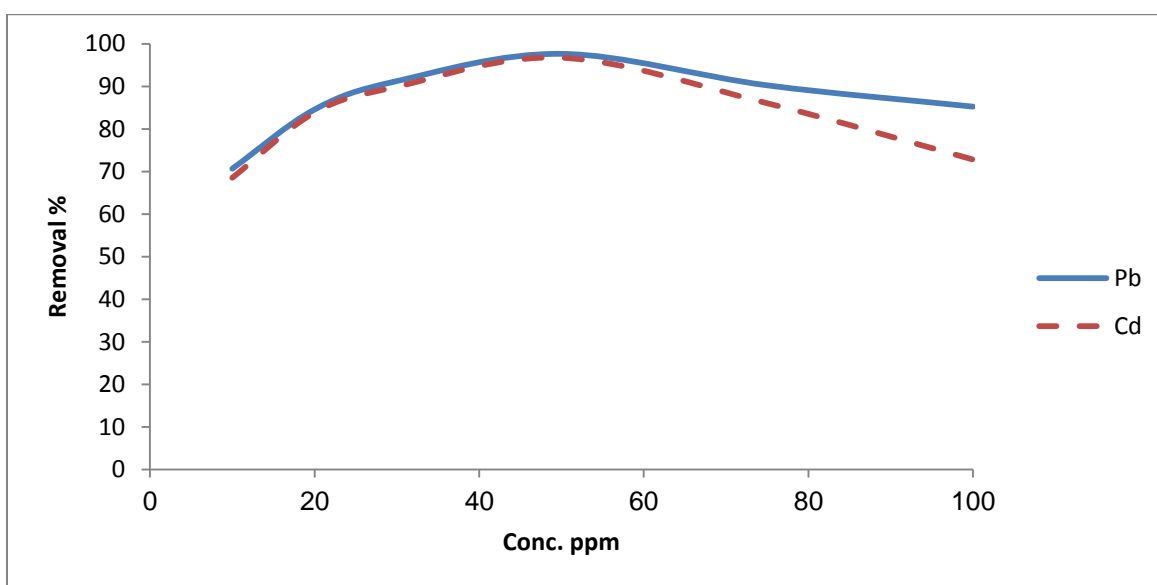

Fig 9. Removal of Cd^{2+} and Pb^{2+} by activated muscovite according to initial metal concentration

3.4.4. Effect of contact time on heavy metals adsorption

In order to determine the optimum contact time to maximum Cd^{2+} and Pb^{2+} adsorption, its value was varied at times 30,60,120, and 240 min in series of experiment, keeping other parameters constant. The effect of contact time on removal of heavy metals was indicated in Figure (10). The result refers to that the best contact time of Cd^{2+} and Pb^{2+} was 60 min for the adsorption on activated Muscovite adsorbent.

4.1.2.2.5. Effect of temperature on heavy metals adsorption

The effect of temperature on the adsorption of Cd^{2+} and Pb^{2+} had been studied with different temperatures (25°C, 35°C, 45°C and 60°C). The results were represented in Figure (11). The results showed that the removal percentage of Cd^{2+} and Pb^{2+} on activated muscovite increased at room temperature.
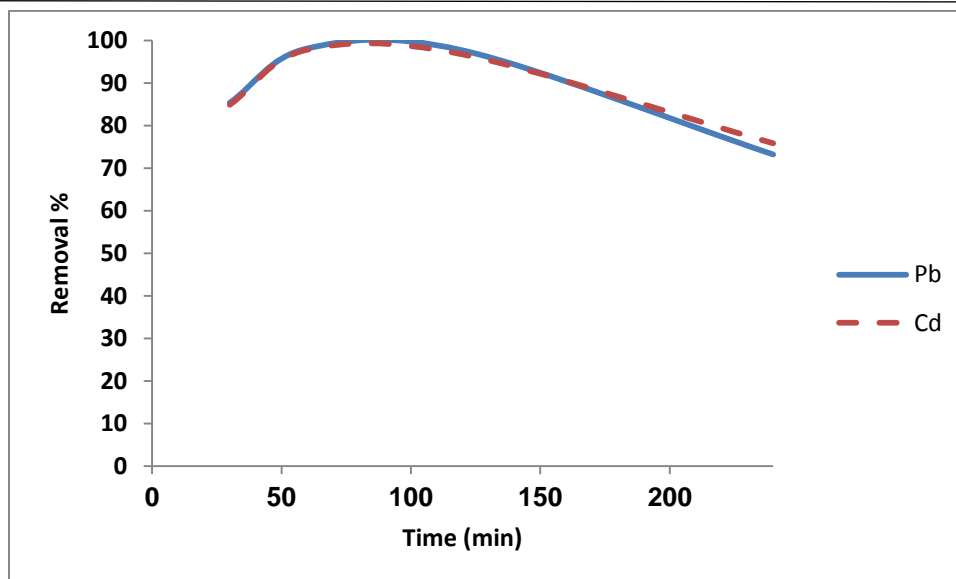
Fig.10. Removal of Cd^{2+} and Pb^{2+} on activated muscovite according to contact time
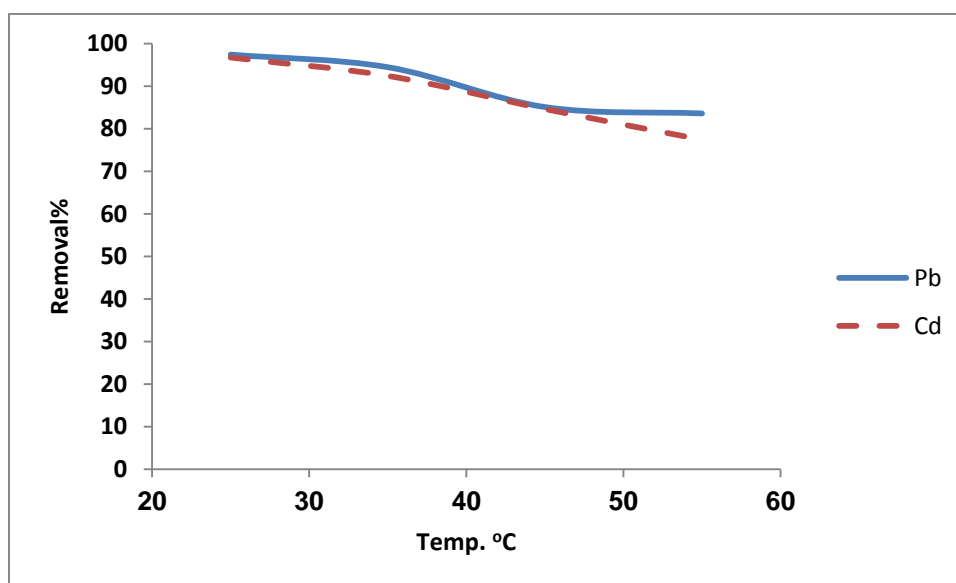
Fig. 11. Removal of Cd^{2+} and Pb^{2+} by activated muscovite according to temperature

2.3.7. Adsorption Isotherm

The experimental data collected at $25^{o}C$ and initial heavy metals concentration of 50 ppm /50 mL with 2 g of activated muscovite at 60 min contact time. The data was fitted into the following isotherms: Langmuir, Freundlich, Temkine and Dubinin-Raduskevich (D-R) isotherm models.

2.3.7.1. Langmuir isotherm

The Langmuir model assumes that the solid surface carries a limited number of sites that are characterized by equal energy of adsorption, independent of the degree of coverage and thus indicating a monolayer adsorption. The linearized form of Langmuir equation is described by equation:

$$C_e/q_e = 1/Q_ob + C_e/Q_o$$

Where C_e , is the equilibrium concentration of heavy metals solution (mg/L), q_e the equilibrium capacity of heavy metals on adsorbent (mg/g), Q_o is monolayer adsorption capacity of adsorbent (mg/g) and b , is the Langmuir bonding energy coefficient (L/mg).

The b and Q_o can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e.

2.3.7.2. Freundlich isotherm

The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process. The empirical Freundlich equation is expressed as:

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

Where $K_{f,}$, is the Freundlich isotherm constant indicating the adsorption capacity and n, is the adsorption intensity. If the 1/n values are below one it indicates a normal adsorption on the other hand 1/n being above one indicates cooperation adsorption. The K_f and n can be calculated from the intercept and slope of the linear plot of log q_e against log C_e.

3.10.3. The Temkin isotherm

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption. Linear form of Temkin equation is expressed as:

$$q_e = B \ln K + B \ln C_e$$

Where B = RT/b, b is the Temkin constant related to heat of sorption. q_e (mg/g) and C_e (mg/L) are the amount of adsorbed heavy metals per unite weight of adsorbent and unabsorbed heavy metals concentration in solution at equilibrium, respectively. Therefore, a plot of q_e versus ln C_e to determine the constant B which is the constant related to the heat of sorption (J/mol) and K, is the Temkin isotherm equilibrium binding constant.

3.10.4. Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Gunay et al., 2007; Dabrowski, 2001). It means that,it is applied to distinguish between physical and chemical adsorption of heavy metals.

The linearized D-R equation (Chen et al., 2008) can be written as:

$$\text{Ln } q_e = \ln q_m - BE^2$$

Where B, is a constant related to the adsorption energy (mol/kJ), q_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g), and E, is the polanyi potential, which can be obtained by following equation:

$$E = RT \ln (1+1/C_e)$$

Where R, is the ideal gas constant (R=8.314 J/mol K) and T is absolute temperature (K).

By plotting ln qe vs E^2, it is possible to determine the value of B from the slope and the value of qm from the intercept, which is ln qm. The mean free energy E (KJ/mol) of sorption can be estimated by using B values as expressed in the following equation (Chowdhury and Saha, 2010).

$$E = 1/ (2B) ½$$

The magnitude of E may characterize the type of the adsorption as chemical ion exchange (E=8-16 kJ /mol), or physical adsorption (E < 8 kJ/mol), (Sivakumar and Rupainwar, 2011)

All of the isotherm model parameters for the adsorption of Pb and Cd are provided in Table 7. As seen from Table 7 in Langmuir isotherm calculated adsorption capacities for cadmium and lead are 22.95 and 23.127 mg/g, respectively.

In the Freundlich isotherm, calculated values of 1/n for cadmium and lead, are 0.1269and 0.2125, respectively, indicates an effective adsorption and also indicates degree of favorability of adsorption. Higher values of K (isotherm equilibrium binding) and lower values of B for cadmium and lead, This means that the adsorption of RB on alum and mud sludge adsorbents follows the Temkin model.

By using D–R isotherm, adsorption energies for cadmium and lead are calculated as 1.58 and 0.316 (kJ/mol). These low values of adsorption energy show that the adsorption has a physical nature.

Table 7. Results of adsorption isotherm parameters for Cd^{2+} and Pb^{2+}

Parameters	Pb	Cd
Langmuir Isotherm model		
Q_0	22.95	23.127
b_L (L/mg)	0.63	0.15
R^2	0.9835	0.9778
Freundlich Isotherm model		
1/n	0.2125	0.1269
K_f ($mg^{-1/n}$ $L^{1/n}$ g^{-1})	17.18	16.22
R^2	0.977	0.9
Temkin Isotherm model		
B (j/mol)	2.34	2.546
b_T	1058.8	973.2
Kt (L/g)	192.2	153.2
R^2	0.95	0.9134
Dubin-Raduskevich Isotherm model		
q_m (mg/g)	17.1	15.74
E (kj/mol)	1.58	0.316
R^2	0.8513	0.9478
B (mol /kJ^2)	$2*10^{-7}$	$5*10^{-6}$

3.11. Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process which provides useful data to improve the efficiency of the adsorption and feasibility of process scale-up (Eftekhari et al., 2010), It means to describe the rate of uptake of heavy metalss onto the

adsorbents and this rate controls the equilibrium time. The kinetics of sorption that define the efficiency of sorption RB heavy metals on Alum and Mud sludge adsorbent were checked by the Pseudo–first order, Pseudo–second order, Intra–particle diffusion and Elovich models.

3.11.1. Pseudo–first order model

The pseudo- first order kinetic model is represented as follows:

$$Log\ (q_e - q_t) = \log q_e - (K_1/2.303)t$$

Where, q_e and q_t (mg/g), are the sorption capacities at equilibrium and time (min) respectively, and K_1, is the rate constant of the pseudo- first order (Kamal et al., 2010; Inbaraj and Sulochana, 2006). A plot of log (q_e-q_t) vs t should give linear relationship with the slop k_1 and intercept of log q_e.

3.11.2. Pseudo–second order model

The linearized form of the pseudo – second order kinetic model is represented as:

$$t/q_t = 1/K_2 q_e^2 + 1/q_e t$$

Where K_2 is the rate constant of pseudo–second order adsorption

A plot of t/q_t vs t shows a linear relationship values of K_2 and equilibrium adsorption capacity q_e are calculated from intercept and slop of the plot. In order to calculate the adsorption rate constants of cadmium and lead, the first order reaction kinetic was applied for both metals Pseudo-second-order kinetic was also applied for the experimental data of each metal.

The values of *q*e calculated are found from the intersection points of the first and second degree reaction kinetic curves. Table (8) presents all of the data.

As the difference between *QE*, calculated and QE, experimental values are considered, it is seen that the Cd^{2+} and Pb^{2+} removal with activated Muscovite is well described by the second order reaction kinetics. Moreover, all the correlation coefficients (R^2) of second order reaction kinetics are higher than that of the first order reaction kinetics.

3.11.3. Intra-particle diffusion model

For solid–liquid, adsorption process, the solute transfer is usually characterized by intra–particle diffusion model was used to identify the mechanism involved in adsorption process:

$$q_t = K_i t^{1/2} + C$$

Where, K_i (mg g^{-1} min$^{-1/2}$), is the rate constant of the intra-particle diffusion model and C (mg g^{-1}) reflects the boundary layer effect. The K_i and C can be determined from the slop and intercept of the linear plot of q_t vs $t^{1/2}$.

The experimental data were used for intraparticle diffusion model, the intraparticle diffusion constant (Kid), intercept and the correlation coefficient (R^2) are calculated.

3.11.4. Elovich model

One of the most useful models for describing such activated chemisorptions is Elovich equation.

The Elovich equation was: $q_t = 1/\beta \ln[\alpha\beta] + 1/\beta \ln t$

Where, α, the initial adsorption β, the adsorption coefficient

The constant α and β are calculated from plots obtained when q_e is plotted vs ln t.

Table (8) Calculated kinetic parameters for the adsorption of Cd^{2+} and Pb^{2+}

Parameters	Pb	Cd
Pseudo first-order		
K_1 $(min)^{-1}$	0.115	0.2
q_e (mg/g)	18.76	20.5
R^2	0.886	0.826
Pseudo second-order		
K_2 (g/mg min)	$5.9*10^{-3}$	$4.6*10^{-4}$
q_e (mg/g)	19.96	14.3
R^2	0.996	0.999
Elovich model		
α (mg/min)	9.2	5.13
β (g/mg)	0.52	0.6
R^2	0.95	0.95
Intra particle diffusion model		
K_{id}	0.54	0.616
C $(mg\ g^{-1})$	5.33	7.28
R^2	0.82	0.82

3.12. Thermodynamics of adsorption

The thermodynamic parameters such as changes in Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) are the actual indicators for particle applications.

Adsorption thermodynamics was evaluated with respect to different temperatures (298, 313, and 333 K).

The thermodynamic parameters were calculated by the following equation:

$$Ln\ K = \Delta S^o/R - \Delta H^o /RT$$

Where, R is the gas constant (8.314 J/mol K) and T is temperature (K)

Both ΔH^o and ΔS^o were determined from the slope and intercept of the van't Hoff plots of ln k vs 1/T (Ozcan et al., 2006; Nollet et al., 2003).

The free energy of specific adsorption $\Delta G0$ (KJ/mol) is calculated from the following expression.

$$\Delta G^o = \Delta H^o - T\ \Delta S^o$$

The estimated thermodynamic parameters are presented in Table (9). The adsorption data indicate that $\Delta G°$ values for cadmium and lead were negative at all temperatures. That negative $\Delta G°$ confirms the spontaneous nature of adsorption of Cd^{2+} and Pb^{2+} by activated Muscovite. The parameter $\Delta G°$ suggests that adsorption of Cd^{2+} and Pb^2 is physical adsorption process. The

positive values of $\Delta H°$ confirmed the endothermic nature of adsorption process. The positive $\Delta S°$ showed increased randomness at the solid–solution interface during the adsorption.

Table (9) Thermo dynamical parameters for the adsorption of Cd^{2+} and Pb^{2+}

Parameters		Cd	Pb
ΔH^o, kJ/mol		20.04	18.87
ΔS^o, J/ mol K		91	75
ΔG^o, kJ/mol	298 k	-6.78	-3.48
	308 k	-7.68	-4.23
	318 k	-8.58	-4.98
	328k	-9.48	-5.73
R^2		0.94	0.95

4. Conclusion

In this study, Effective adsorbent was prepared Muscovite by activation with H_2O_2, HCl and/or H_2O_2 / HCl, in which the most effective activator for the removal of Pb and Cd was H_2O_2 / HCl . The results of batch Pb and Cd adsorption experimental studies reflected that the adsorption operation depends on pH, contact time, adsorbent dose, intial metal concentration, and solution temperature. The adsorption kinetics of lead and cadmium ions followed the pseudo second-order kinetic model. The linearadsption isotherms models were used to represent the experimental data, and the Langmuir model fitted well the metal adsorption. The negative value of ΔG^o and ΔS^o showed that the adsorption of the lead and cadmium ions by Muscovite adsorbent. The simple, clean, and green procedure of this adsorbent would offer a vital technique for industrial wastewater cleanup.

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