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RESEARCH ARTICLE

Removal of cadmium, lead, zinc, copper and iron from their aqueous solution by kaolinite clay

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Abstract

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This study includes the removal of some heavy metals such as Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) in aqueous solution using kaolinite clay. The adsorption of these metals on kaolinite conformed to linear form of Langmuir adsorption equation. Langmuir C_m constant for each metal were found as 35.7mg/g (Pb), 16 mg/g(Cd), 24.4mg/g(Fe), 12.5mg/g(Zn) and 8mg/g(Cu) at 25 °C respectively. The effect of contact time (5-90min), pH (2-12), temperature (25-60°C), amount of adsorbent (0.05-1.4g) and metal ion concentration (0.5-12ppm), were studied. The optimum conditions were recorded in each case and the adsorption was in the order Pb (II) > Fe (III) > Cd (II) > Zn (II) > Cu (II). The thermodynamic parameters such as ΔH , ΔG and ΔS were calculated and these values shown that the adsorption of heavy metals on kaolinite was an endothermic process, and the adsorption was of physical type, which increase by temperature rises. Also the kinetic parameter such as adsorption rate constant (k) was calculated. The desorption process was studied for each metal, and the effect of regeneration time on efficiency of the uptake percentage was represented and discussed.

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INTRODUCTION

Water is the most essential substance for all life on earth and a precious resource for human civilization. Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the 21st century (1). Water pollution by heavy metals is a worldwide environmental problem and results in serious threats to ecosystem and human health. Heavy metals may come from various industrial sources such as electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramic and glass industries. Lead, cadmium and copper are common contaminants of industrial wastewaters. Because they pose serious environmental problems and are dangerous to human health, considerable attention has been paid to methods for their removal from industrial wastewaters. These toxic heavy metals, especially Pb^{2+} and Cd^{2+} , can be accumulated in bone, brain, kidney and muscles and may cause brain, bone, liver and kidney damage, also dysfunction of the central nervous system in human beings due to their cumulative effects. Since the heavy metal pollutants are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders even at very low concentrations (2). Heavy metals can be distinguished from three other toxic pollutants. Although Cu^{2+} and Zn^{2+} are known to be the essential trace elements to humans, but higher Cu^{2+} and Zn^{2+} intake can also cause adverse effects. The maximum acceptable concentration of Pb^{2+} , Cd^{2+} and Cu^{2+} recommended by the World Health Organization (WHO) for drinking water are less than 0.01, 0.003 and 2 mg/L, respectively, while that of Zn^{2+} for drinking water at levels above 3 mg/L, may not be acceptable to consumers (2). There have

been many studies on the removal of heavy metals from water and wastewater using chemical precipitation, physical treatment such as ion exchange, solvent extraction, reverse osmosis and adsorption (3). Among them, reverse osmosis, although it is very effective, is a cost-prohibitive process as the membranes get easily spoiled requiring frequent replacement. Chemical precipitation however is not very suitable when the pollutants are present in trace amounts and also a large amount of sludge is produced. Ion exchange is expensive and sophisticated. Solvent extraction or electrolytic processes are also available but they are considered to be cost-effective only for more concentrated solutions (4). Adsorption is one of the most popular methods for the removal of heavy metals from the water and waste water. Natural clays as the adsorbent with a low cost have received much attention on heavy metals sorption from contaminated water. Clay minerals have different adsorption capacities for metal ions, such as mesoporous silica, and montmorillonite clay for Hg (II), which depend on the absorption conditions, as they have been found to be very effective, economical, versatile and simple (5). The removal of metal ions using kaolinite clay is based on ion exchange and adsorption mechanisms, and kaolinite has a relative low cation-exchange capacity (CEC) [3–15 meq/100 g of clay] and smaller surface area ranged from 10 to 20 m²/g. There are many researchers studied kaolinite clay for the removal of heavy metals from aqueous solution, such as adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite Clay (6). Kaolinite was used for the removal of copper, nickel, cobalt and manganese from aqueous solution (7), also removal of Pb²⁺, Cu²⁺, Fe³⁺, Mn²⁺ and Zn²⁺ from aqueous solution at different conditions have been studied (8). Many of clays were used for the removal of heavy metals from aqueous solution using adsorption mechanism like (attapulgite) to get rid of some toxic ions (9), Egyptian montmorillonite as an adsorbent (10), and glauconitic clay (11) are also used. Clays such as kaolinite can be modified to increase its surface area and hence the adsorption capacity (12, 13). In our study we investigate the suitable conditions to remove Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) from aqueous solution by adsorption on natural kaolinite clay. The effect of temperature, contact time, pH, metal ion concentration and amount of adsorbent were performed. The adsorption and desorption process were studied, and some of the physicochemical parameters involved were determined. The mechanism of the adsorption process on kaolinite clay was related to the surface property of the kaolinite.

2.1 .Material and methods

2. 1.1. Adsorbent

Kaolinite clay was provided from Sigma Company (Germany). It was parched at 60°C for 24 h and sieved to pass 200µm mesh size and then kept in the bottle. Investigate of the kaolinite by X-ray fluorescence was done, and the data was indicated in Table.1. Similar results were presented by Kamel et al. (8).

Table 1: X-ray analysis of kaolinite clay

Metal oxide	K ₂ O	TiO ₂	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
ppm	1.07	2.3	21.5	6.5	4.00	11.1

2. 1.2. Adsorbate

A stock solution of each metal was prepared by dissolving a calculated weight of metal salts in sufficient amount of deionized water, to obtain the required concentration. All chemicals used were of analytical pure grade. Stock solutions of the investigated metals, were prepared using the salts Cd (NO₃)₂, ZnCl₂, (CH₃COO)₂Pb, CuCl₂, and FeCl₃. The pH of the solution was adjusted by using 0.1M NaOH and/or 0.1M HCl. For the preparing (100 ppm) from metal ions 0.1849 g was taken from (CH₃COO)₂Pb.3H₂O (Assay 99%), 0.2710 g CuCl₂.2H₂O (Assay 99%), 0.2934 g FeCl₃ (Assay 99.5%), 0.2148 g ZnCl₂ (Assay 97%) and 0.1114 g from Cd(NO₃)₂ (Assay 99%).

2. 1.3. Adsorption process

The experiments of the adsorption technique were performed at room temperature (25°C) using 50 ml capped borosilicate bottles containing 20ml of metal ion solution and 0.2 g of the adsorbent (kaolinite clay) ,after agitation the suspensions were centrifuged for 10 min at 2500 rpm and the filtrate or supernatant was taken for the

analysis by an atomic absorption spectrophotometer (AAS), to determine the concentration of the heavy metals. Various conditions affected on the adsorption process, such as contact time, pH, metal ion concentration, temperature, and amount of adsorbent, were studied.

2. 1.4. Desorption study

The aim of the use of clay to the lack of cost, so underestimate cost more to re-use the clay again. Regeneration of the clay depends on the binding affinity between metal ion and the clay surface (5), capacity for hydroxylation, ionic potential, electro- negativity, softness, and position as in the Irving–Williams series (14). Using 30ml borosilicate bottle it was added 20ml (2M) HCl to 0.2 g kaolinite clay fully loaded with 30 mg/l of metals Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) the bottles were shaken at required temperature using immersed water bath for a required time to attain the equilibrium, then the equilibrium concentration of heavy metals was determined by an atomic absorption spectrophotometer.

2.2. Instruments

- Atomic absorption spectrophotometer (AAS,) model varian (EL07083665).
- Centrifuge model 800, China.
- Magnetic stirrer model Wheaton Rc-2 (10371203) ,Japan.
- X-Ray model (X-Strata 920) IEC62321, Taiwan.
- pH meter model (ML 1010), Romania.

3. Results and discussion

3. 1. Equilibrium Contact time influence

The contact time for the adsorption of Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) was investigated at different time intervals in the range of 5-90 min, as shown in Fig.1. From the experiments, it was found a variation of the uptake percent of the selected ions. After equilibrium the metal ions were separated by centrifuge and determined by atomic spectrophotometer (15). By referring to Fig.1 it is noticed that the adsorption process is directly proportional with the contact time, until reached to the equilibrium. As the adsorption take place by the attraction between the positive cation from the bulk liquid phase, and the negative vacant adsorption sites (16) as these sites decrease the adsorption decrease hence the uptake percent decrease until consistency , The equilibrium was attained after 30 min for Pb (II) (92.5%), Fe (III) (91.1%) and cd (II) (88.1%), but for Zn (II) (87.8%) was after 45 min, and for Cu (II) (73.9%) was after 15 min .From the data illustrated by Fig .1, the adsorption process was very fast and equilibrium was attained after shaking for 30 min. The order of the uptake capacity of these metal ions was Pb (II)>Fe (III)>Cd (II) > Zn (II)>Cu (II). So the kaolinite clay showed strong affinity of adsorption, and preference for Pb (II) than for Cu (II) as was resulted from the differences in ion-exchange capacities when different metal ions absorbed on the kaolinite clay as represented by Saha et al. (17).

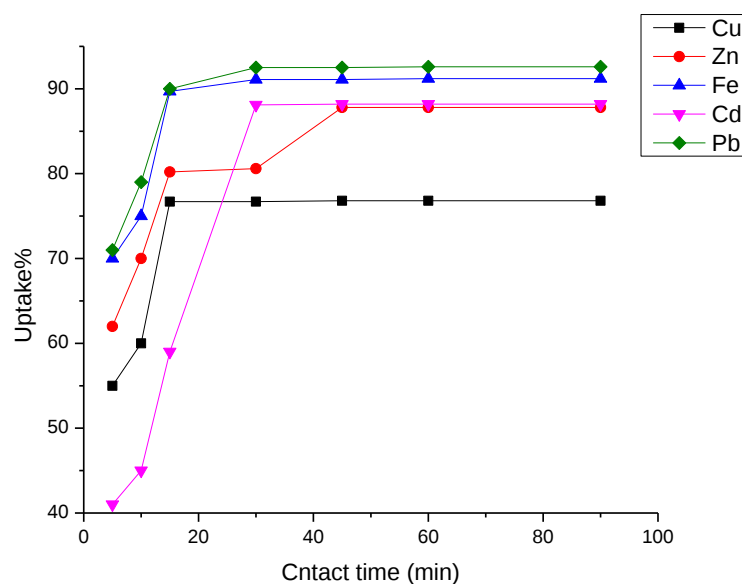


Fig 1. Contact time influence on the uptake of cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) at concentrations 0.620,2.00,0.5137,4.661 and 7.6 ppm respectively; dose of adsorbent 10 g/L; temperature 25°C and solution volume 20ml.

3. 2. Kinetics of adsorption

By using the equation $C_r = C_i e^{-kt}$ where C_r is the residual concentration of heavy metal ions, C_i is the initial metal concentration, k and t represents adsorption rate constant and time, respectively. The equilibrium time attained after 1h Fig.2 shows the kinetic curves adsorption of Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) at 25°C and 40°C, k values were calculated by plotting $\ln C_r$ versus t and the values are Summarized in Table. 2. The values of adsorption rate constants indicate that adsorption was in order Pb (II) > Fe (III) > Cd (II) > Zn (II) > Cu (II).

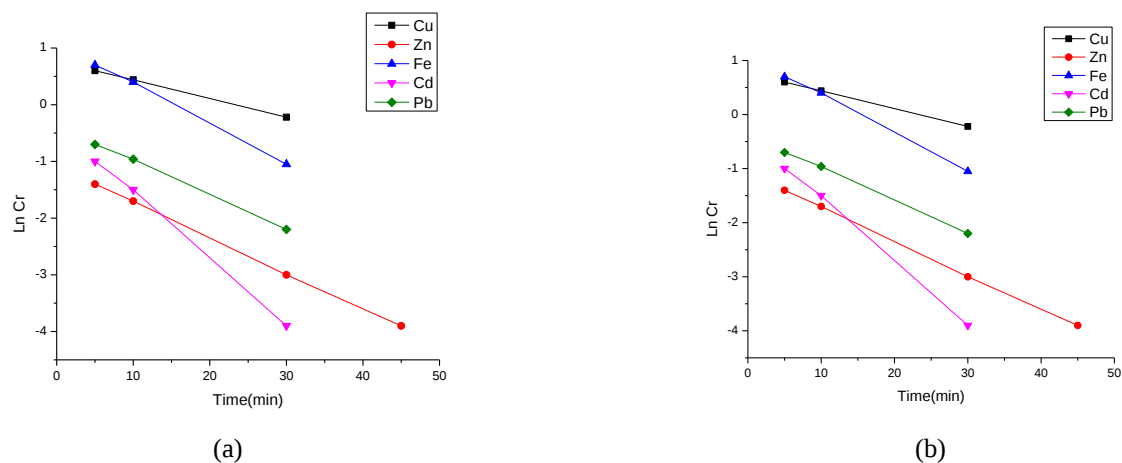


Fig 2. First-order kinetical curves of heavy metal adsorption by kaolinite from aqueous solution at 25°C (a), and, 40°C (b).

Table 2: Values of adsorption rate constant of heavy metals by kaolinite from aqueous solution at 25°C and 40°C.

Metal ion	$k \times 10^3 \text{ (min}^{-1}\text{)}$	
	25°C	40°C
Cu	2	2.4
Zn	3.2	4.1
Cd	3.8	5.2
Fe	5	6.4
Pb	7.6	9.6

3. 3. Effect of pH

This study was investigated by varying pH values of the solution from 2-12 .The pH were adjusted using 0.1M NaOH and/or 0.1M HCl .By reference to the Fig .3. It is observed that the uptake percent was directly proportional to pH, as it increases the adsorption will increase until reached to the maximum values. That was meant that adsorption increases as pH increase from 2 to 7 except Cu (I) was attained to maximum uptake at pH =8. Table .3 summarized the maximum uptake values for Cd (II), Pb (II), Zn (II), Fe (III) and Cu (I) which were 91.9%, 95%, 85.13% and 94.2% and 79.5% respectively at their suitable pH values. As the nature of the kaolinite clay surface there were number of active sites carry negative charge such as aluminol (Al-OH) or silanol (Si-OH) the electrostatic attraction was performed between these sites and the positive ions (heavy metals) (18). Therefore as pH decreases the solution become acidic so the concentration of (H^+) increase and hence competition between (H^+) and cations at the negative sites increases, hence the adsorption decreases, and vice versa at the high pH values(19) .

Table 3: A suitable pH values, for the removal of Cd (II), Pb (II), Zn (II), Cu (I) and Fe (III) from aqueous solution.

Metal ion	Cu	Zn	Fe	Cd	Pb
PH	8	7	7	7	7
Max.uptake	79.5	85.13	94.3	91.9	95.1

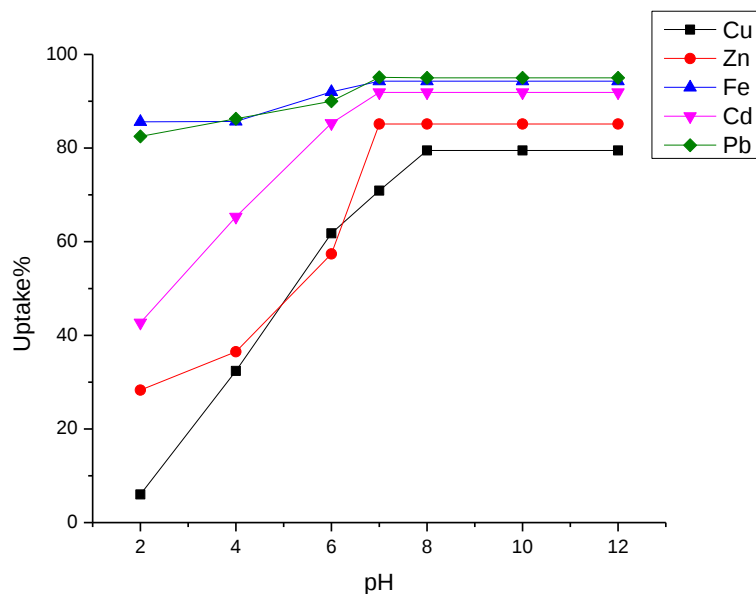


Fig 3. pH influence on the uptake %, of Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) at concentrations 0.620,2.00,0.5137,4.661 and 7.6 ppm respectively; dose of adsorbent 10 g/L; temperature 25°C; solution volume 20ml and contact time 1h.

3. 4. Influence of metal ion concentration

This variable was studied to determine a suitable concentration which can be used to give high uptake values.

Table 4: Relation between metal ion concentration (ppm). and uptake%, at pH=7, amount of adsorbent,0.2g, solution volume,20ml ; temperature 25°C and contact time 1h.

Cation	Initial conc.	Final conc.	Uptake%
Cu(II)	2.8	0.76	72.9
	4.7	1.3	72.3
	6.9	2.6	62.3
	9.6	2.6	72.9
Zn(II)	0.52	0.074	85.7
	0.6	0.078	87
	0.73	0.12	83.5
	0.84	0.15	82.2
Fe(III)	7.6	0.51	93.3
	9.2	0.7	92.3
	11.7	1	91.4
	13.5	1	92.6
Cd(II)	0.62	0.07	88.7
	0.85	0.11	87
	1.2	0.17	85.8
	1.8	0.17	88.8
Pb(II)	2.2	0.09	95.7
	4.1	0.17	95.8
	6.3	0.27	95.7
	7.2	0.3	95.8

Table 5: Relation between metal ion concentration (ppm), and uptake%, at pH=7, maamount of adsoebant=0.2g, solution volume=20ml; temperature 40°C and contact time 1h.

<i>Cation</i>	<i>Initial conc.</i>	<i>Final conc.</i>	<i>Uptake%</i>
Cu(II)	2.8	0.7	75
	4.7	1.2	74.4
	6.9	2.4	65.2
	9.6	2.5	74
Zn(II)	0.52	0.07	86.5
	0.6	0.08	86.7
	0.73	0.1	86.3
	0.84	0.12	85.7
Fe(III)	7.6	0.48	93.7
	9.2	0.65	92.9
	11.7	0.9	92.3
	13.5	1	92.6
Cd(II)	0.62	0.06	90.3
	0.85	0.09	89.4
	1.2	0.15	87.5
	1.8	0.17	90.5
Pb(II)	2.2	0.08	96.3
	4.1	0.15	96.3
	6.3	0.25	96
	7.2	0.27	96.25

The data presented in the Table 4 and 5 indicates the relation between metal concentration and the uptake%, at 25°C and 40°C respectively. It is observed that at constant amount of adsorbent the uptake% decrease by increasing the metal ion concentration until reaching to the stability as lowest concentration. These because the constant amount of adsorbent (kaolinite) contains specific vacant active sites which were attracted to metal ions even access to the saturation. Therefore by increasing the concentration the amount of ions sorbed on clay increase even be constant. Also the uptake % increases as raising the temperature from 25°C to 40°C, due to the increase of kinetics of ions to be adsorbed.

3. 5. Effect the amount of adsorbent

This study was aimed to remove high concentration of metal ions, by minimal quantities of adsorbent. The kaolinite clay could remove the metals Cd(II), Pb (II), Zn (II), Cu (II) and Fe (III) by adsorption on the vacant active sites which located on its surface, until sites be saturated then the adsorption will be constant. The adsorption sites were non-uniform, and nonspecific in nature. It was in conformity with the existence of different types of possible adsorption sites on clay surface, with considerable difference in energy depend on where site was on an edge or was located in a defect position (5). From Fig .4 it was clear that the adsorption process of the metal ions increase with increasing the amount of adsorbent to reach a nearly saturation level at about 10 g/l.

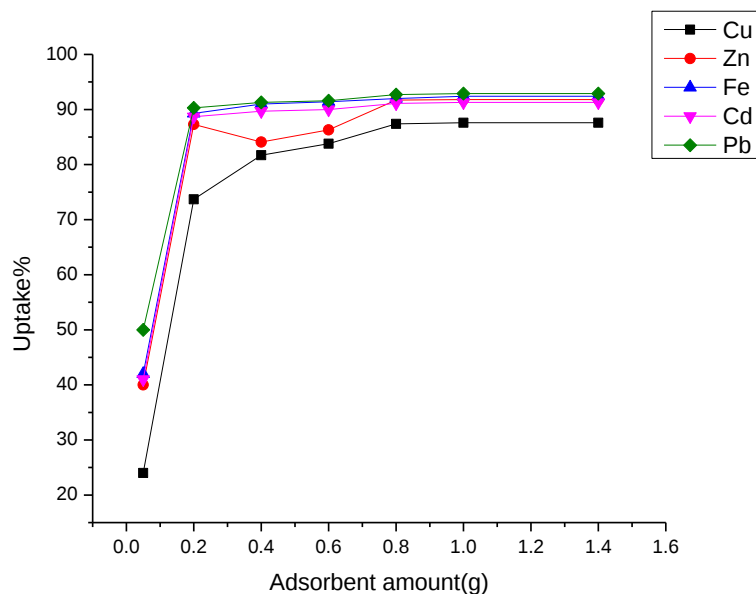


Fig 4. Influence of adsorbent amount on the uptake %, of Cd (I), Pb (I), Zn (I), Cu (I) and Fe (III) at concentrations 0.620,2.00,0.5137,4.661 and 7.6 ppm respectively; dose of adsorbent 10 g/L; temperature 25°C; solution volume 20ml and contact time 1h.

3. 6. Temperature influences

In this study the temperature influence was from the range 25-60°C as shown in Fig .5. It is clear from the figure that the uptake of the heavy metals Cd (I), Pb (I), Zn (I), Cu (I) and Fe (III) was in order Pb (I)>Fe (III)>Cd (I) > Zn (I)>Cu (I) as was mentioned previously. However the uptake% was little increase with temperature rising.

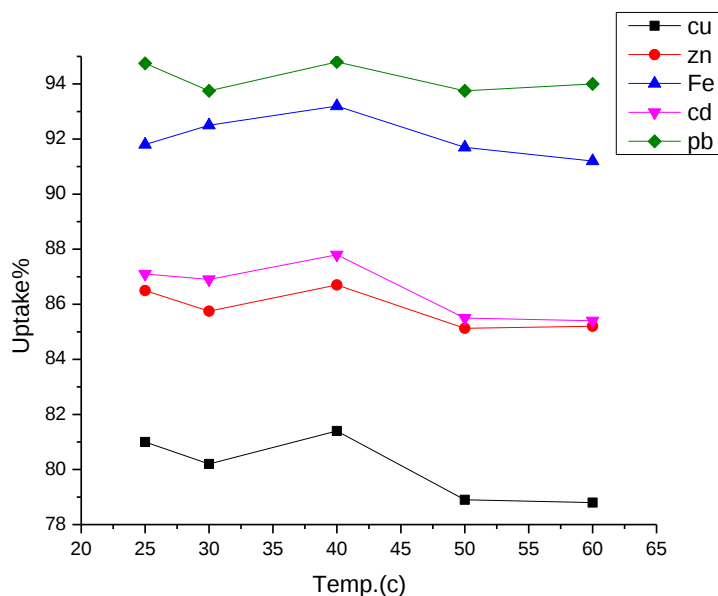


Fig 5. Temp. influence on the uptake of Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) at concentrations 0.620,2.00,0.5137,4.661 and 7.6 ppm respectively; dose of adsorbent 10 g/L; solution volume 20ml and contact time 1h.

3.7. Adsorption isotherms

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherms can be generated based on theoretical models where Langmuir and Freundlich models are the most commonly used ones (12). From Fig.6 adsorption isotherms of heavy metals from aqueous solution on the kaolinite at 25°C and 40°C were observed. These isotherms satisfy Langmuir's adsorption isotherms. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

To quantify the adsorption capacity of the kaolinite for removal of heavy metal ions, the Langmuir linear adsorption equation was applied in the form equation (1)

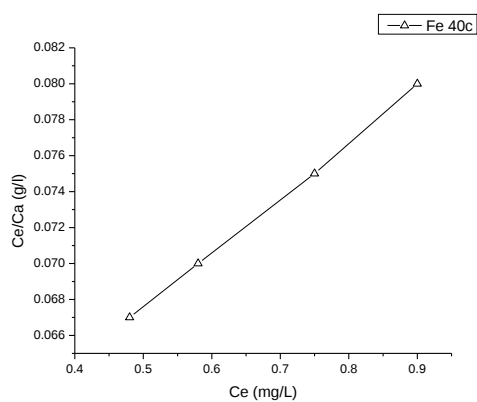
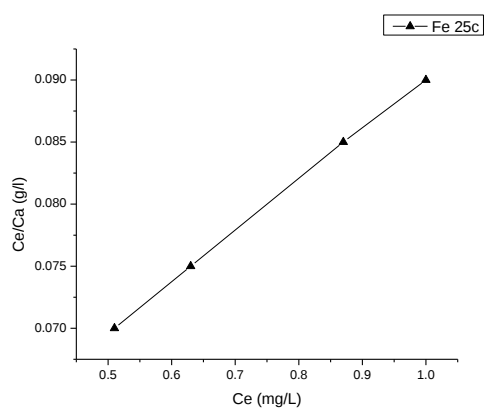
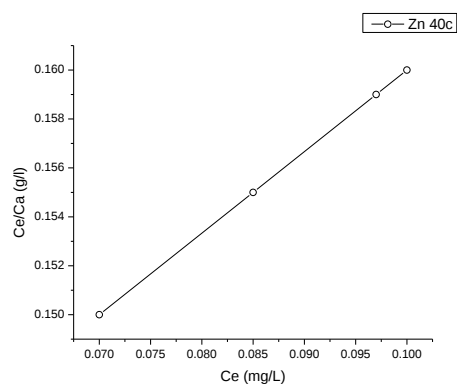
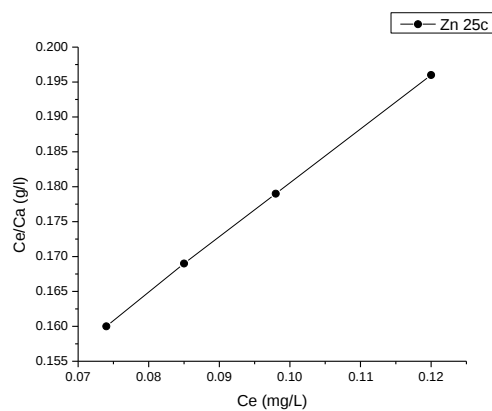
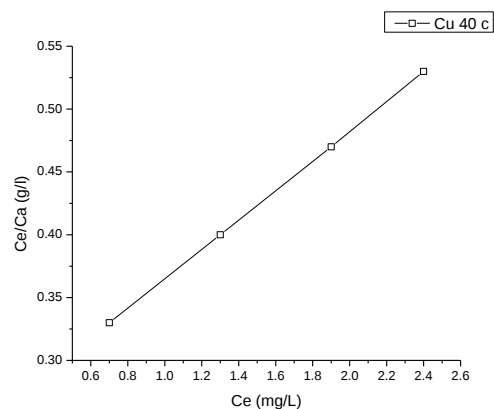
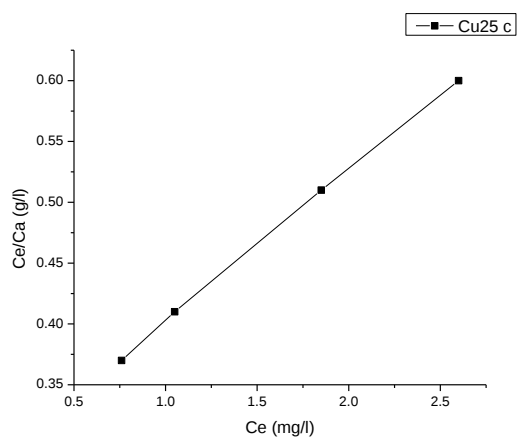
$$C_e/C_a = (1/bC_m) + (C_e/C_m) \dots\dots\dots (1).$$

Where C_e is the equilibrium concentration of adsorbate, b is the constant of the Langmuir isotherm related to the equilibrium constant or binding energy, C_a is the amount of adsorbed ions (mg/g) and C_m is the amount of maximum adsorbed. From Table.6 the value of b and C_m are increase with temperature in the order Pb (II) > Fe (III) > Cd (II) > Zn (II) > Cu (II). Kaolinite is a representative layered aluminosilicate mineral with the structure of the tetrahedral (Si centre) and octahedral (Al centre) sheet in a 1:1 ratio. The permanent structural charge of kaolinite is minor, hence cation adsorption take place mainly at the proton bearing surface functional group such as silanols and aluminols exposed at the edge of the sheets. Because formation of stable complex (between silanol or aluminol and heavy metal cations) facilitates ability of adsorption of heavy metals, this causes high value of b constant. Increase of b with temperature shows that there is a chemical interaction between adsorbent and adsorbate (7). Thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) for using heavy metal ions adsorption by kaolinite were calculated using the following equations:

$$\ln b = \ln b' - \Delta H/RT \dots\dots\dots (2)$$

$$\ln b = - \Delta G/ RT \dots\dots\dots (3)$$

$$\Delta S = (\Delta H - \Delta G)/ T \dots\dots\dots (4)$$



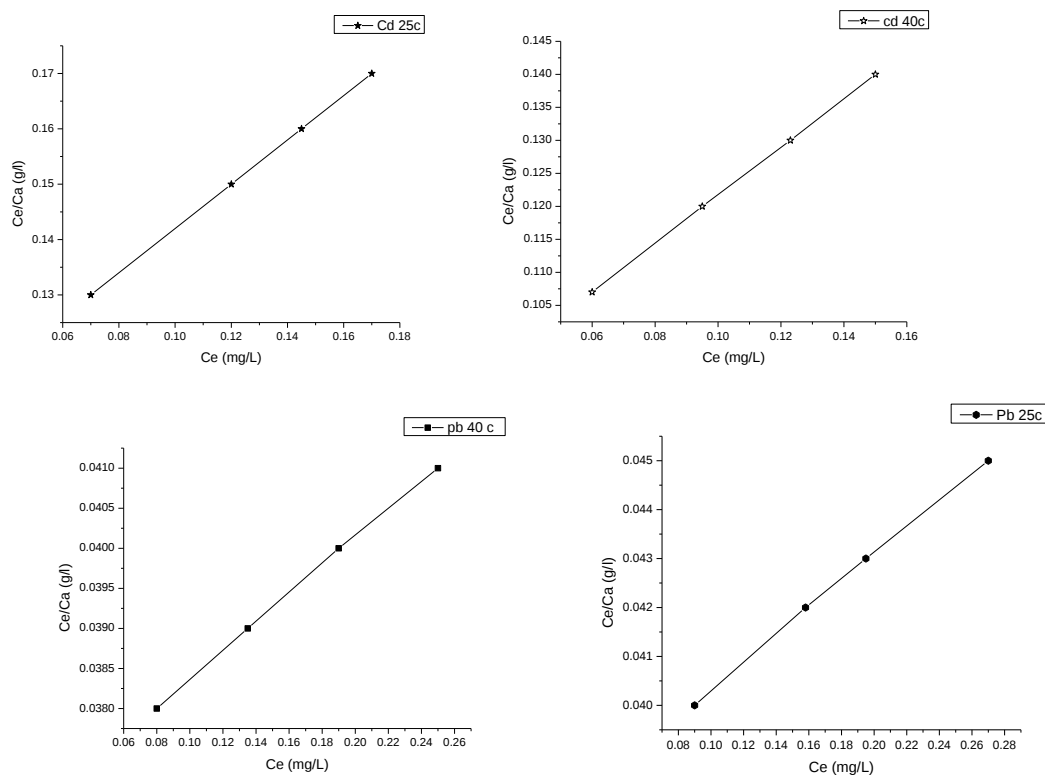


Fig 6. Langmuir isotherms, for the dsorption, of different heavy metal ions on kaolinite, at 25°C and 40°C.

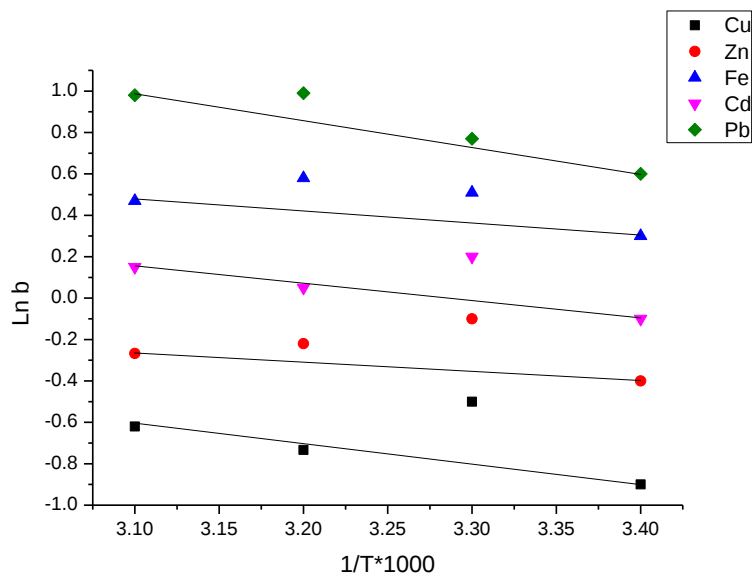


Fig 7. Variation of $\ln b$, with reciprocal of temperature.

From Fig.7 the enthalpy change(ΔH) is determined graphically by plotting $\ln b$ versus $1/T$, which gives a straight line, then the free energy (ΔG) and entropy(ΔS) were calculated and presented in Table .6. The free energy change (ΔG) was small, positive and decreases with increasing the temperature;therefor the better adsorption is obtained at higher temperature. The positive values of entropy may be due to some structural changes in both the adsorbates and adsorbents during the adsorption process (7).

Table 6: Values of Langmuir constants, and thermodynamic parameters for the adsorption of metal ions.

Metal ions	Cm(mg/g)		b(L/mg)		ΔH (kJ/mol)	ΔG (kJ/mol)		ΔS (kJ/mol)
	25°C	40°C	25°C	40°C		25°C	40°C	
Cu	8	8.3	0.45	0.48	12.1	10.13	9.1	0.12
Zn	12.5	14	0.7	0.8	18.8	13.9	12.2	0.24
Fe	24.4	33.3	1.35	1.8	34.9	21.4	20	0.78
Cd	16	19	0.9	1.06	19.7	14.2	12.9	0.3
Pb	35.7	48	1.96	2.7	38.4	23.6	21.7	0.9

3. 8. Desorption study

The results of desorption process (using 2M HCl), indicated that the desorption was almost the reverse of adsorption process, where adsorption was in order Pb (II)>Fe (III)>cd (II) > Zn (II)>Cu (II), therefor Pb (II) ions was greater affinity for kaolinite clay than Cu (II), while desorption data indicated that Cu (II) was greater desorption %, were used for regeneration of the loaded kaolinite clay were magnesium chloride or sodium chloride or hydrochloric acid (20).

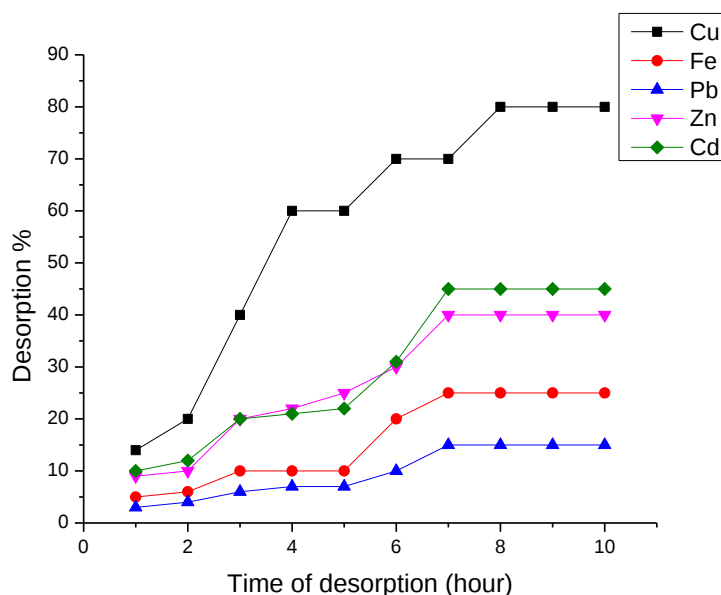


Fig 8. Desorption process of metals cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) from kaolinite clay surface after 10 hours using initial conc. 30 ppm in the presence of (2M) HCl.

As shown in Fig.8 it was clear that the desorption percent of Pb (II) was lower than desorption percent of Cu (II) due to the high affinity between Pb (II) and kaolinite clay than these between Cu (II) and kaolinite clay. Also due to that more Pb (II) ions were adsorbed on specific sites than on the non specific sites, where the Cu (II) ions were only adsorbed on non specific sites. In the regeneration process using HCl(2M) the heavy metal ions Cd (II), Pb (II), Zn(II), Cu (II) and Fe (III) loaded on the clay can be replaced by H⁺ ions to form H- kaolinite which can be used for further sorption investigations. By reference to Fig.9 we noticed that the uptake percent of heavy metals is inversely proportional with the number of regeneration cycle.

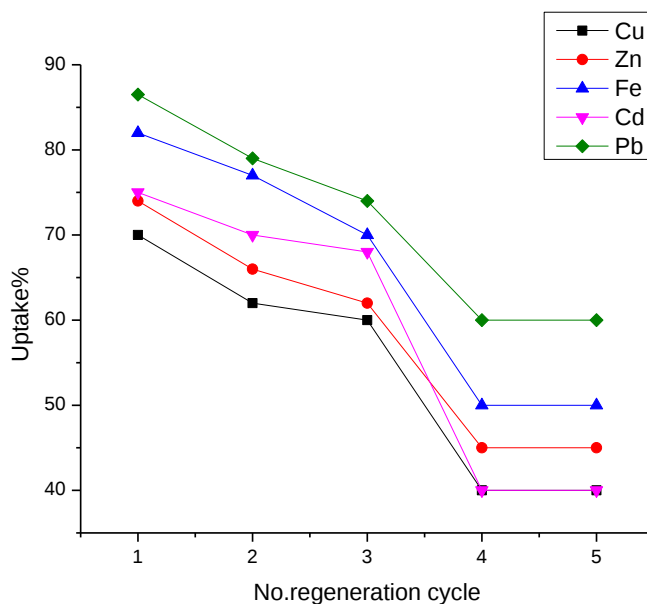


Fig 9. The effect of number of regeneration cycle on the uptake % of Cd (II), Pb (II), Zn (II), Cu (II) and Fe (III) onto kaolinite clay surface.

Conclusions

From the presented data the kaolinite clay was used successfully for the removal of heavy metals Cd(II), Pb (II), Zn (II), Cu (II) and Fe (III) from their aqueous solution. The removal of these metals by kaolinite clay was performed by ion exchange and adsorption mechanism. The adsorption capacity was in order Pb (II) > Fe (III) > Cd (II) > Zn (II) > Cu (II). There are many factors affecting on the adsorption process such as contact time, pH, metal ion concentration, amount of adsorbent and temperature. Thermodynamic data refer to low heat of adsorption, positive values of Gibbs free energy and low positive values of entropy, which reveal that the adsorption was of physical type, and endothermic reaction. As the future of this work, kaolinite clay will be used for the removal of heavy metals from contaminated river waters.

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