Studies on the adsorption characteristics of some heavy elements using Vermiculite

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Abstract: The uncontrolled release of liquid wastes into the environment may lead to hazard to the human and the environment. There have been extensive studies for development of various technologies for removal of Cd^{2+} and Co^{2+} from wastes The removal of Cd^{2+} and Co^{2+} ions from aqueous solution by Vermiculite has been investigated. The Vermiculite was characterized by Particle size, Surface area, and chemical analysis. The adsorption behavior of Vermiculite has been studied as a function of the solution agitation time, pH, initial metal concentration in solution, particle size, and temperature. Kinetic studies were undertaken to show the mechanistic aspects of the process. It was showed that the process was first order reaction for the two metal ions. Sorption data have been correlated with both, Langmuir and Freundlich adsorption models. Thermodynamic parameters such as ΔH^o, ΔS^o, and ΔG^o were calculated from the slope and intercept of linear plot of $\ln K_D$ against $1/T$. The ΔH^o and ΔG^o values of metal ions adsorption on the two adsorbents show endothermic heat of adsorption. But there is a negative free energy value, indicating that the process of ions adsorption is favored at high temperatures.
[A. A. Ezz El-Deen , S. A. Waly , K. A. EL.Adham , A. M. Dakroury and M. M. Shoukry. **Studies on the adsorption characteristics of some heavy elements using Vermiculite.** *J Am Sci* 2012;8(7):247-255]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 39

1. Introduction

The liquid wastes containing Cd^{2+} and Co^{2+} are generated from different activities such as industry, medicine, agriculture and research. The mobility of trace metals and radionuclides released into aquatic and torrential environments by mining, industrial processes, and municipal waste disposal practices are an area that deserves significant scientific, public health, and regulatory attention. The U.S. Environmental protection Agency includes cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc on its priority pollutant list for waste effluent [1].

The uncontrolled release of liquid wastes into the environment may lead to hazard to the human and the environment. For this reason, the wastes should be safely managed according to the regulatory requirements. Waste management includes collection, treatment, conditioning, storage and disposal [2].

Several treatment technologies have been developed for eliminating heavy metal from solution such as chemical precipitation, ultra filtration, adsorption and ion exchange. Among these methods, adsorption and ion exchange using natural, synthetic and modified inorganic and organic solids have been explored [3].

In this work, we show the application of vermiculite in the removal of Cd and Co from liquid waste. ^{60}Co is generated from nuclear power reactors as fission product or through corrosion and activation of structural materials .Cobalt-60 is made artificially and has many common industrial applications such as in leveling devices, thickness gauges and in radiotherapy in hospitals. Large sources of cobalt-60 are increasingly used for sterilization of spices and certain foods. Cobalt-60 is also used for industrial radiography to detect structural, Cobalt-60 sealed sources presents an external gamma hazard.

Cadmium is produced commercially as special form sources for x-ray fluorescence spectrometry analysis, thickness gauges and scientific research, cadmium cause kidney damage and destruction of lung tissues. Cd and its compounds are toxic by ingestion and inhalation. The oral toxicity of Cd and its compounds is high. However, ingestion causes a strong emetic action, little Cd is therefore absorbed and fatal poising rarely occurs. Cd and some compounds are suspected carcinogens.

Removal of this element has been an important issue in waste management. A natural inorganic substance such as clay minerals act as potential ionic exchangers for heavy metals due to their low cost, high abundance, easy manipulation, and harmlessness to the environment [3, 4]. Several investigations have been made to assess their ability to adsorb toxic elements, rare earth elements and heavy metals or to improve their effectiveness [5].

Vermiculite was the clay mineral chosen for heavy metal adsorption. It is classified as 2:1 type and it has been explored with the aim of evaluating structural changes, adsorptive, catalytic and electrochemical properties [3].

Clay mineral can remove pollutants from aqueous solution owing to their high cation exchange capacity and high specific surface area associated with their small particle sizes. It is well known that vermiculites have very high cation exchange capacities, in the range of 100to 150 mill equivalent grams per 100 grams of clay due to the substitutions of Mg^{2+} and Fe^{2+} in place of Al^{3+} in the octahedral positions and, to a higher degree, to substitutions of Al^{3+} in place of Si^{4+} in the tetrahedral positions. More over, they swell less than smectites because of their higher charge in the tetrahedral sheets and possess higher elasticity and plasticity than kaolin and mica. These properties make them particularly suitable as low-cost natural sorbents for the treatment of the waste. Vermiculite, as the smectites having similar structural arrangement, can adsorbed heavy metal via two different mechanisms: (1) cation exchange at the planar sites, resulting from the interaction between metal ions and negative permanent charge (outer-sphere complexes) and (2) formation of inner-sphere complexes through $Si-O^-$ and $Al-O^-$ groups at the clay particle edges. Both mechanisms are pH dependent but the later is particularly influenced by pH because in acid condition (pH< 4) most silanol aluminol groups o edges are protoned [4, 6].

The aim of this work is the removal of some heavy element such as Co and Cd from liquid waste by vermiculite. The main aim of this research program is to study and investigate the following points; Study of physical and chemical properties of the used material. Investigate sorption capabilities of this used material, and the effect of the following parameters: time, pH, particle size of the material, concentration of ion and temperature. Evaluations of experimental results and investigate the possibility of developing mathematical models to predict the sorption behaviors of the used materials.

2. Experimental
2.1 Materials.
Vermiculite obtained from El-nasr for fertilizer and Phosphate Company. The vermiculite was washed with de-ionized water to remove foreign materials, dusts and fines then dried at 120°C. The heated product was cooled then sieved before use. The hydrate chloride salt of $Co^{2+}$and the hydrate nitrate salt of Cd^{2+} were supplied by Merck as laboratory analytical grade reagents.

2.2. Instrumentation
Inductive Coupled Plasma–Atomic Emission Spectroscopy (JY138) was used for elemental analysis, X-ray diffraction patterns model PW/1710 was used to provide chemical composition, and surface area was obtained using Gemini 2360 V5.00

Micrometric Instrument USA, Density was obtained using Accupyc 1330 Density analyzer Micrometric Instrument USA, Hanna instrument pH meter, and Thermostatic shaker.

2.3. Batch mode adsorption studies
Batch experiments were carried out in polypropylene bottles at ambient temperature using a definite volume of ion solutions with known initial concentration mixed with a definite amount of vermiculite. The mixture was shaked for a certain time at 25 °C, using a controlled temperature shaker bath. At the end of the shaking period, the samples were filtered through Whatman no.1 filter paper, the supernatant solutions and the residual concentrations were determined using ICP-AES. The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required.

2.4. Removal and adsorption of Heavy Metals:
The percent heavy metal removal was calculated using the following equation:

$$\% R = \frac{C_o - C}{C_o} *100 \qquad (1)$$

Where:
C_0 : Initial heavy metal ion concentration of test solution, mg/l.
C : Final equilibrium concentration of test solution, mg/l.
The adsorbed capacity was calculated using the following equation

$$q = (C_o - C) * \frac{v}{m} \qquad (2)$$

Where:
q :is the amount of heavy metal ions adsorbed per unite mass of adsorbent in, mg/g
V: is the volume of the solution in, L
M: is the weight of dry adsorbent in, g

3. Results and discussion
The experiments were done to investigate the removal of Cd^{2+} and Co^{2+} ions through adsorption on vermiculite. And studies the factors affecting in the adsorption process.

3.1 Characterization of the adsorbent
The original vermiculite sample was characterized by X-ray diffraction patterns, a philips x-ray diffraction equipment model PW/1710 with monochromator, cu-radiation(λ=1.542Å)at 40 KV,30MA and scanning speed 0.02°/sec. were used. The chemical composition of vermiculite are given in

table(1).and X-ray diffraction patterns for original vermiculite sample were illustrated in Fig. (1). And the surface area of vermiculite using Gemini 2360 is 1 m^2/g and density is 2.8 g/cm^3.

Table (1): Chemical constituent of vermiculite using X-ray diffraction

Constituents	Chemical composition(%)
SiO$_2$	35.05
Al$_2$O$_3$	14.55
MgO	21.71
FeO	5.13
K$_2$O	8.31
CaO	0.78
TiO$_2$	1.02
Na$_2$O	0.11
Loss of ignition	14.12
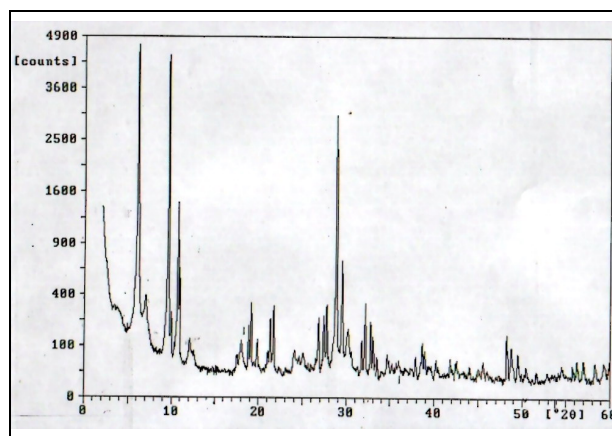
Fig. (1) X-ray diffraction pattern for original vermiculite sample.

3.2. Effect of Agitation Time on the Removal of Cd^{2+} and Co^{2+}Ions

The effect of agitation time on the removal of Cd^{2+}and Co^{2+}ions from aqueous solution is shown in Fig.(2). It is clear from figure the removal of the metal ions increases as the agitation time increases. The equilibrium was attained after 4h for the two metal ions on vermiculite. It can be seen that there is a rapid sorption of Cd^{2+} and Co^{2+} ions in the initial stages of equilibrium followed by saturation. Therefore in each experiment the shaking time was set for optimum time.
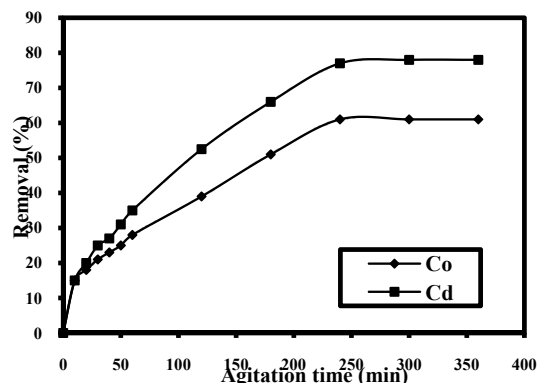

Fig. (2): Effect of agitation time on removal % of Cd^{2+}and Co^{2+} ions adsorbed on vermiculite (Initial Conc=100ppm;PH=7.2 and T=25 ^{o}C)

3.3. Effect of Initial Metal Ion Concentration.

The effect of initial Cd^{2+} and Co^{2+}ions concentrations was studied using different concentrations (50, 100 and 200 ppm). Figs. (3, 4) show the effect of the variation of the initial Cd^{2+} and Co^{2+}ions concentration on the percentage removal. There is a sharp initial increase achieving almost a constant value within 4 hours. The time necessary for attainment of saturation remains unaffected at all concentrations. The smooth and continuous curves reached complete equilibrium in 4 hrs, and the extent of adsorption remained practically constant for even an extended period of contact (24 hrs).This suggests that the adsorption of cadmium and cobalt ions occurs in a single step and is not accompanied by any complexity i.e. this type behavior indicates that the adsorption process is first- order [7]. it was found from Fig. (3, 4) that the percentage removal increases from 60 % to 92% and from 44%to 73.4% for Cd^{2+} and Co^{2+} ions on vermiculite respectively, with an increase in the bulk dilution from 200 to 50 ppm. This increase in percentage adsorption is due to the availability of the larger number of surface sites of the adsorbent for a relatively smaller number of adsorbing species at higher dilution [7].
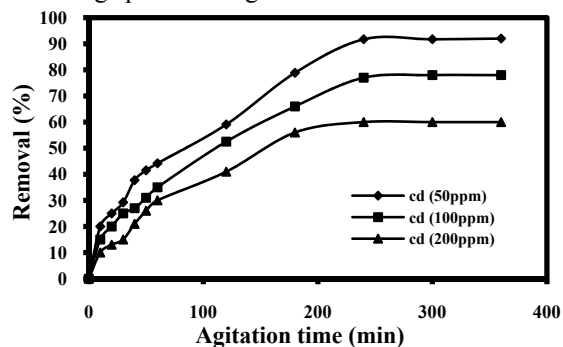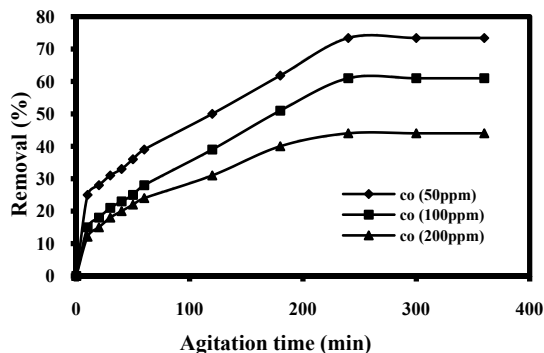

Fig.(3)Time variation of adsorption of Cd^{2+} ion on vermiculite at various Conc. of Cd^{2+}.

Fig.(4) Time variation of adsorption of Co^{2+} ion on ve

3.4 Effect of variation of particle size on the removal of Cd^{2+} and Co^{2+}ions

The results for the removal of Cd^{2+} and Co^{2+}ions as a function of particle size are shown in fig. (5, 6).it can be noted that the decrease in the particle size of vermiculite results in an increase in the rate of adsorbate removal. This can be attributed to the increase in the available specific surface area of contact.

The effect of variation of particle size was studied using different particle sizes of vermiculite (80,250,400 μm).
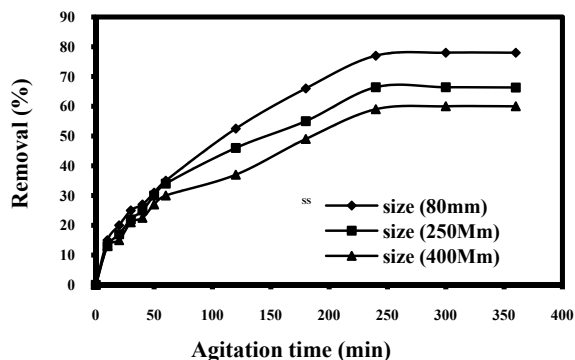
Fig. (5): Effect of particle size of vermiculite on the removal % of cd^{2+} (Intial cd^{2+} Conc=100ppm, pH=7.2, equilibrium time=4h at T=25 °C)
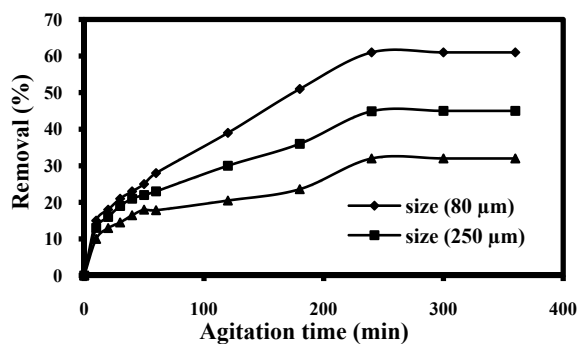
Fig. (6): Effect of particle size vermiculite on the removal % of co^{2+}ions. (Intial co^2 Conc=100ppm, pH=7.2, equilibrium time=4hrs at T=25 °C)
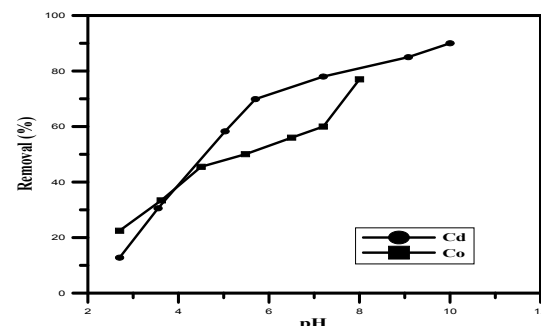
3.5. Effect of pH
3.5.1 Effect of pH on the removal of Cd^{2+} ion.

The results of the effect of pH on the sorption of Cd^{2+} ion by vermiculite are shown in Fig.(7). This effect is important in establishing the optimum sorption of metal ions at the solids/liquid interface. In the beginning, the solution pH was observed to be in the range of 6.8–7.6. A series of dilute HNO$_3$and NaOH solution was prepared and added drop by drop during pH adjustment to ensure minimum increase in the solution volume. This study was carried in the pH range (2–10) as the metal solutions were precipitated above pH 11[8].

Fig. (7) shows that at pH 2.7 the sorption was about 13% by vermiculite. By increasing the pH by 2 units, the uptake increased to about 58.27%. This sharp increase in the sorption efficiency could be explained in two ways. Firstly, at low pH, high concentrations of H$^+$ ions were present in solution that competes for vacant adsorption sites of adsorbent. This phenomenon could be confirmed by the observation of sharp increase in the final solution pH of those having low initial pH values. Secondly, for each hydrolysable metal ion, there was a critical pH range (often 2 units wide) where the metal uptake efficiency increased from a very low level to maximum value. This pH value is commonly called as the adsorption edge. For vermiculite, pH adsorption edge was 3–5. After pH 5, the sorption increased gradually up to pH10. The optimum uptake of 90% was observed at pH 10.

3.5.2 Effect of pH on the removal of Co^{2+} ion.

The effect of pH on the sorption of Co^{2+} ion by vermiculite could be important in establishing the optimum sorption of metal ion at the solids/liquid interface and the results are shown in Fig. (7). This study was carried in the pH range (2–8) as the metal solutions were precipitated above pH 8.5[9]. It's clear from the figure that, the removal percentage of the Co^{2+} ion on vermiculite was found to be increased with increasing pH.

Fig. (7): Effect of pH on the adsorption of Cd^{2+} and Co^{2+} on vermiculite at equilibrium.

3.6 Effect of Temperature Variation on the removal of Cd^{2+} and Co^{2+} ions

The temperature is an important parameter so the effect of temperature was studied at different temperatures (298,313and 333 K). Fig.(8, 9) show the considerable effects of temperature on the adsorption of Cd^{2+} and Co^{2+} ions from solution at different temperatures (298, 313and 333 K). It can be seen that as the solution temperature increases, the adsorption increases. This can be explained by the fact that by increasing the temperature of the solution, the kinetic energy of the adsorbate particles will increase so the velocity of the adsorbate molecules will increase, this increase in velocity will lead to decrease the time needed by these particle to reach the adsorbent surface so the rate of adsorption will increase. This indicates that the adsorption process is mainly chemisorption accompanied by a chemical reaction. Fig. (8, 9) show that % removal increases by increasing the temperature. The removal rate from the solution increases by increasing metal ions solution temperature in the studied temperature range.
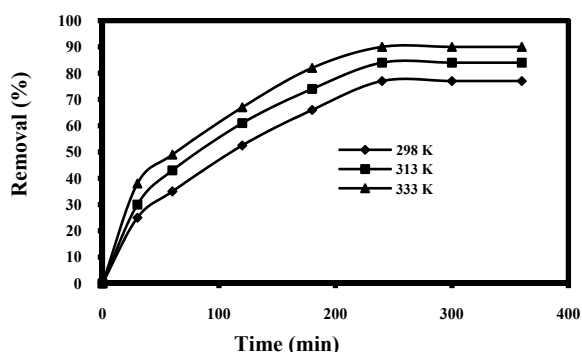

Fig.(8): Effect of temperature on the removal (%) of Cd^{2+} ions adsorbed by vermiculite. (Intial cd^{2+} Conc=100ppm;pH=7.2;equilibrium time =4hrs)
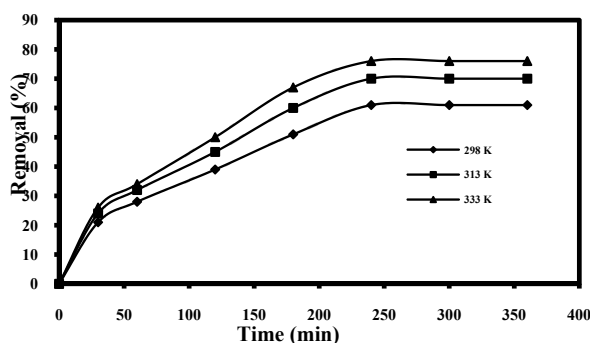

Fig.(9) Effect of temperature on the removal (%) of Co^{2+} ions adsorbed by vermiculite. (Intial co^{2+} Conc=100ppm, pH =7.2, equilibrium time =4h)

3.7.1. Effect of temperature on rate constants

The effect of temperature on reaction rates is well known and important in understanding reaction mechanisms. Svante Arrhenius, a Swedish physical chemist who received the 1903 Nobel Prize for chemistry, noted that for most reactions, the increase in rate with increasing temperature is nonlinear [10]. Drawing upon work by van't Hoff (1884) for the decomposition of chloracetic acid in an aqueous solution, Arrhenius (1889) published his famous paper ''Ober die Reacktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren'' in which he derived an expression for the kinetic temperature dependence of reactions. He concluded that most reaction-rate data obeyed the equation:

$$k = A\ e^{-Ea/RT} \qquad (3)$$

Where k is the rate constant, A is the frequency or pre-exponential factor, Ea is the activation energy, R is the gas constant [8.31451 J (mol K^{-1})], and T is the absolute temperature in Kelvin. The frequency factor is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction. As the magnitude of Ea increases, k becomes smaller. Thus, reaction rates decrease as the energy barrier increases.

Taking the natural log of both sides of Eq. (3) one obtains:

$$\ln k = -Ea/RT + \ln A \qquad (4)$$

By plotting $\ln k$ vs. $1/T$, a linear relationship is obtained and one can determine Ea from the slope (-Ea/R) and A from the y-intercept. This equation assumes that Ea and A are constants or nearly constants with respect to temperature.

Energies of activation below 42kJ mol^{-1} generally indicate diffusion-controlled processes and higher values represent chemical reaction processes. In terms of Ea, diffusion- or transport controlled reactions are those governed by mass transfer or diffusion of the sorptive from the bulk solution to the sorbent surface and can be described using the parabolic rate law. Conversely, the reaction is surface-controlled if the reaction between the sorptive and sorbent is slow compared with the transport or diffusion of the sorptive to the sorbent. For surface-controlled reactions, the concentration of the sorptive next to the sorbent surface is equal to the concentration of the sorptive in the bulk solution and the kinetic relationship between time and sorptive concentration should be linear [10]. Fig. (10, 11) show the apparent first-order kinetic plots of Cd^{2+} and Co^{2+} ions sorption on vermiculite and at three different temperatures.

The rate constants for the adsorption of Cd^{2+} and Co^{2+} ions on vermiculite are calculated from the Fig.(10,11). and tabulated in Table (2).

Figs.(12,13) showed the linear plot between lnK and 1/T. The activation energies (Ea) calculated from the slope of the linear plot between lnK and 1/T were found to be 1.6 KJ mol^{-1} for Cd^{2+}ions on vermiculite and 12.7 KJ mol^{-1} for Co^{2+}ions on vermiculite .one sees a range in Ea values from 1.6 to 21 KJ mol^{-1} and as noted elier, Ea values <42 KJ mol^{-1} generally indicate diffusion-controlled processes.

Table (2) apparent first-order sorption rate constants for cadmium sorption at three temperatures on vermiculite

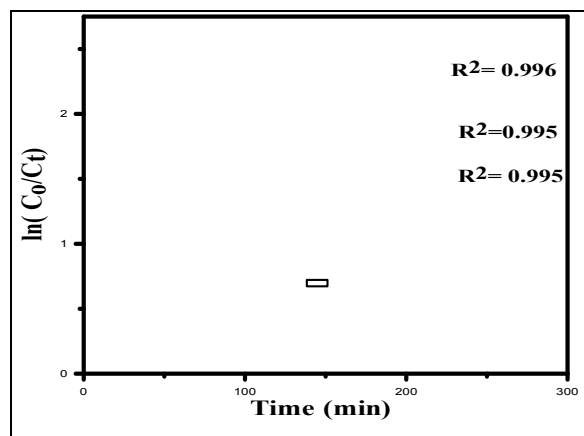| Adsorbent	Temperature (K)	K for Co (s^{-1})	K for Cd (s^{-1})
Vermiculite	298	6.65 x 10^{-5}	1.018 x 10^{-4}
	313	8.43 x 10^{-5}	1.271 x 10^{-4}
	333	9.93 x 10^{-5}	1.596 x 10^{-4}

Fig. (10): Apparent first–order kinetic plot of Cd^{2+} adsorption on vermiculite at different temperatures.
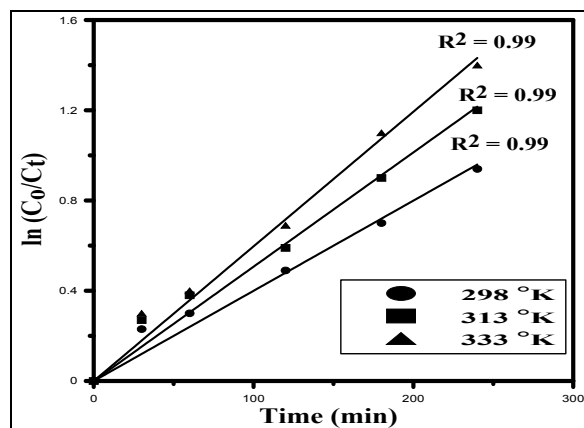

Fig. (11): Apparent first-order kinetic plot of Co^{2+} adsorption on vermiculite at different temperatures.
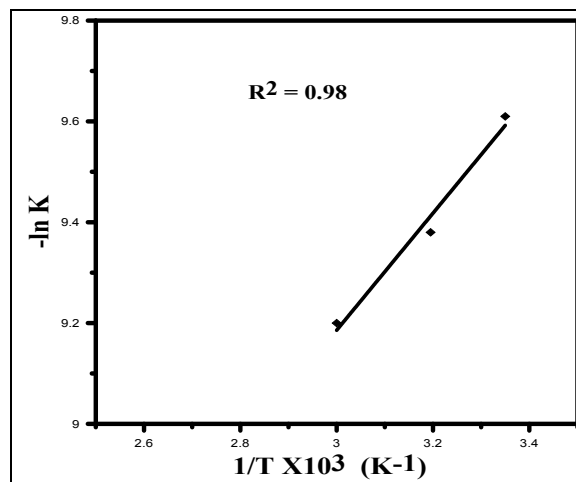

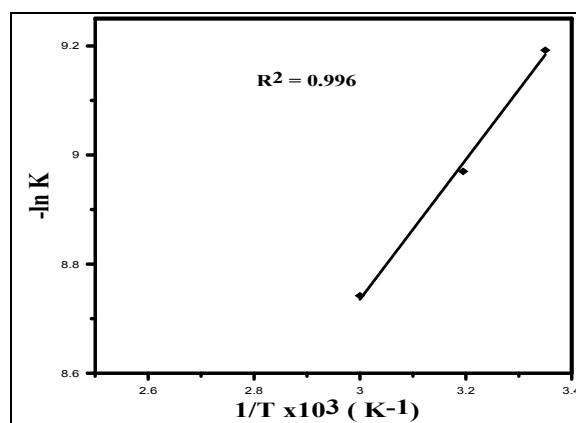Fig.(12):Arrhenius plot of Cd^{2+}ions sorption on vermiculite at different temperatures.

Fig.(13):Arrhenius plot of Co^{2+}ions sorption on vermiculite at different temperatures.

3.8 Equilibrium Isotherm

The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

3.8.1 Langmuir isotherm[11]

Langmuir isotherm is one of the most known models that frequently employed for determination of adsorption parameters.
The Langmuir equation (Eq. (3)), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q^o} + \left(\frac{1}{bQ^o}\right)\left(\frac{1}{C_e}\right) \dots\dots\dots\dots\dots (5)$$

Where: q_e= the amount of solute adsorbed per unit weight of adsorbent.

C_e= equilibrium concentration of the solute.

Q^o= amount of solute adsorbed per unit weight of adsorbent required for monolayer of the surface, also called monolayer capacity.

b = a constant related to the heat of adsorption;
b α exp (-ΔH/RT)

Fig.(14) were showed the Langmuir isotherms of the sorption of Cd^{2+} and Co^{2+} ions on vermiculite. The values of monolayer capacity (Q^o) and Langmuir constant (b) have been evaluated from the intercept and the slope of these plots and given in Table (3)

Table (3) Langmuir constants for the heavy metal ions removal on vermiculite adsorbent at 25 ^{o}C

Heavy metal	Q^o(mgg^{-1})	b(lmol^{-1})	R_L	R^2
Cd	12.55	0.098	0.09	0.97
Co	10.548	0.036	0.217	0.98

The effect of isotherm shape has been discussed [12] with a view to predicting whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed in terms of R_L a dimensionless constant referred to as separation factor or equilibrium parameter.
R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_o}$$ ………………………………. (6)

The value of R_L indicates the type of the isotherm to be irreversible (R_L =0), favorable (0< R_L <1), linear(R_L =1) or unfavorable(R_L >1).
As the RL values lie between 0 and 1, the adsorption isotherm is favorable [12].

3.8.2 Freundlich isotherm[13]

Freundlich isotherm is one of the most known models that frequently employed for determination of adsorption parameters. The Freundlich equation is represented by:
log q_e =log K_f +1/n log C_e………………………….(7)

The amount adsorbed at equilibrium (q_e) is plotted against equilibrium bulk concentration (C_e) and the relationship is found to be linear figure (14), which clearly indicates the applicability of the Freundlich equation for the adsorption of Cd^{2+} and Co^{2+} ions on the adsorbent. This straight line with a slope of 1/n and an intercept giving the value of log Kf .The intercept is roughly an indicator of sorption capacity and the slope of adsorption intensity.

Fig.(15) illustrate the linear plot of Freundlich equation and the adsorption parameters calculated from these figures are summarized in Table (4).

Table(4) Freundlich adsorption parameters for the heavy metal ions removal on vermiculite adsorbent at 25 ^{o}C.

Heavy metal	logK_f	1/n	R^2
Cd	0.38	0.36	0.98
Co	0.005	0.47	0.98
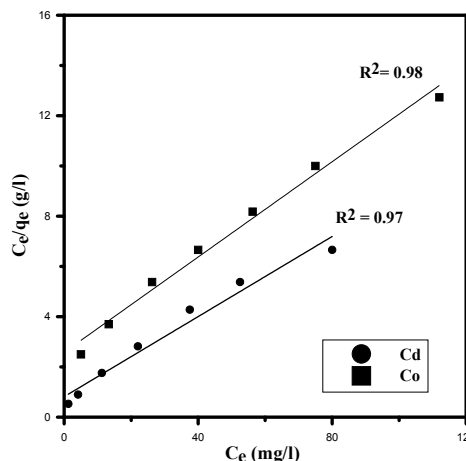
Fig.(14) :Langmuir adsorption isotherm of Cd^{2+} and Co^{2+} on vermiculite at 25 ^{o}C.
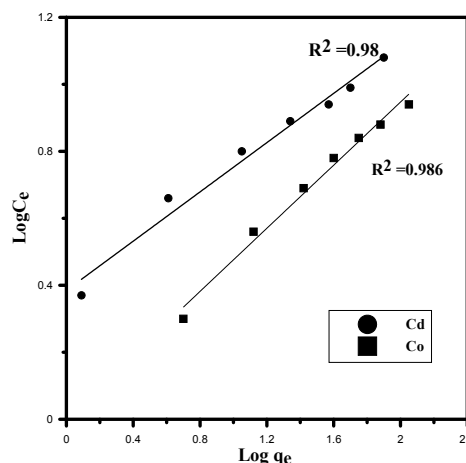

Fig.(15): Freundlich adsorption isotherm of Cd^{2+} and Co^{2+} on vermiculite at 25 ^{o}C.

3.9 Thermodynamic

The experiments were carried out at 298, 313, and 333 K for a metal ions concentration of 100 mg l^{-1}. The distribution coefficient (K_D) values increased with temperature, indicating the endothermic nature of adsorption. The values of ΔH^o and ΔS^o were calculated from the slopes and intercepts of linear regression of lnK_D versus $1/T$ (the values of lnK_D versus T are shown in Fig. (15):

$$K_D = \frac{amount\ of\ metal\ in\ adsorbent}{amount\ of\ metal\ in\ solution} \frac{V}{W} \dots (8)$$

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$ …………………........ (9)

Where K_D is the distribution coefficient (cm3 g^{-1}), ΔS^o is standard entropy, ΔH^o is standard enthalpy, T is the absolute temperature (K), and R is the gas constant (KJ mol^{-1} K). The standard free energy values were calculated from
$\Delta G^o = \Delta H^o - T \Delta S^o$……………………………. (10)

Where ΔG^o is the standard Gibbs free energy. The values of ΔH^o, ΔS^o and ΔG^o are given in Tables (5,6).

As seen in Tables., ΔH^o is positive because the adsorption reaction of metal ions on vermiculite is endothermic. The free energy values for all the systems are negative and the decrease in the value of ΔG^o with increase in temperature show that the reaction is easier at high temperature. Cd^{2+} and Co^{2+} ions in aqueous media are salts of metal or inorganic metal. When the ions get absorbed onto the adsorbent surface, water molecules previously bonded to the metal ion get released and dispersed in the solution; this results in an increase in the entropy.

Table (5): Thermodynamic parameters for the adsorption of Cd^{2+} ion on Vermiculite at different temperatures

Adsorbent	Temperature (K)	ΔG^o (KJ mole^1)	ΔS^o (KJ mole^1)	ΔH^o (KJ mole^{-1})	R^2
Vermiculite	298	-12.67	1..37	266	0.99
	313	5.59			
	333	5.1			

Table (6) Thermodynamic parameters for the adsorption of Co^{2+} ion on Vermiculite at different temperatures

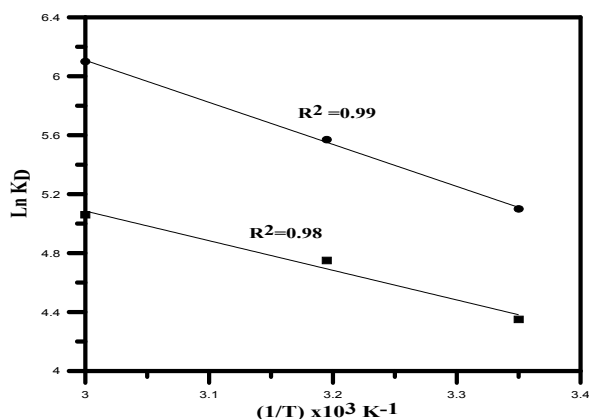| Adsorbent	Temperature (K)	ΔG^o (KJ mole^1)	ΔS^o (KJ mole^1)	ΔH^o (KJ mole^{-1})	R^2
Vermiculite	298	6.32	0.2	97.7	0.98
	313	5.59			
	333	5.1			

Fig. (15): Plot of ln K_D versus (1/T) for Cd^{2+co} and Co^{2+} ions adsorbed on vermiculite.

4. Conclusion

In this study, batch adsorption experiments were performed to evaluate the use of vermiculite as an adsorbent for Cd^{2+} and Co^{2+} ions. From the results obtained in this study, the following conclusions were deduced:

1. The kinetic studies indicated that equilibrium in the adsorption of Cd^{2+} and Co^{2+} ions on vermiculite was reached at 4h of contact time.
2. The adsorption of the ions increased with an increase in the concentrations of these metals in solution.
3. The decrease in the particle size of the material results in an increase in the rate of adsorbate removal. This may be attributed to the increase in the available specific surface area of contact.
4. Metal ions removal efficiency was enhanced by increasing pH of the solution.
5. The kinetics of the adsorption process follows first order rate low.
6. The adsorption behavior of the two metal ions were obeyed both Langmuir and Frundlich isotherms.
7. As temperature increases, the adsorption increases. This can be explained by the fact that by increasing the temperature of the solution, the kinetic energy of the adsorbate particles will increase so the velocity of the adsorbate molecules will increase, this increase in velocity will lead to decrease the time needed by these particle to reach the adsorbent surface so the rate of adsorbate removal will increase. This indicates that the removal process is mainly chemisorption accompanied by a chemical reaction.
8. Thermodynamic parameters such as standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated for predicting the nature of adsorption.
9. It was found that the rate constants were 1.02×10^{-4} for Cd^{2+} ions and were 6.65×10^{-5} for Co^{2+} ions on vermiculite.

10. Activation energies values below 42 kJmol^{-1} generally indicate diffusion-controlled processes and higher values represent chemical reaction processes. The activation energies (E_a) calculated from the slope of the linear plot between lnK and 1/T were found to be 6.51 KJ mol^{-1} and 20.66 KJ mol^{-1} for Cd^{2+} and Co^{2+}ions on vermiculite respectively.

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5/5/2012