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Adsorption of Cobalt (II) ion from Aqueous Solution on Selected Iraqi clay surfaces

امتزاز ايون الكوبلت من محاليله المائية على سطح أطيان عراقية مختارة

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Abstract:-

This work is concerned with one of application of adsorption from solution. It deals with the study of adsorption of Cobalt (II) ion on the surfaces of Attapulgite, bentonite, and kaolin, which are provided locally in Iraq. The purpose of this study is searching for surfaces that are highly applicable for Cobalt (II) ion adsorption to treat the pollution of aqueous solution in nature by this heavy metal ion .This study also involves the feasibility of using (NH_4SCN) (Ammonium thiocyanate) for Visb-spectrophotometric determination of Cobalt (II) ion and to determine the relation between the adsorption quantity of Cobalt (II) ion and equilibrium concentrations (adsorption isotherm) in different conditions of temperature ,ionic strength ,pH , practical size , and adsorbent weight .

الخلاصة

تناول هذا البحث احد تطبيقات ظاهرة الامتزاز من المحلول .حيث تم دراسة امتزاز ايون الكوبلت على سطح أطيان الاتابلكايت و البنتونايت و الكاؤلين المتوافرة محلياً في العراق ، لغرض البحث عن أسطح ذات قابلية عالية لامتزاز ايون الكوبلت بهدف معالجة تلوث المحاليل المائية في الطبيعة بايون هذا العنصر الثقيل . كما وتضمنت هذه الدراسة إمكانية استخدام الكاشف ثايوسيانات الامونيوم NH_4SCN في التقدير الطيفي لعنصر الكوبلت وبرسم العلاقة بين كمية المادة الممتزه (ايون الكوبلت) و التركيز عند الاتزان تم التعرف عل ايزوثيرمات الامتزاز في ظروف مختلفة من درجات حرارة و شدة أيونية و دالة حامضية وحجم دقائق ووزن السطح الماز .

Introduction:-

There are many studies of adsorption in different field such as medicine, pollution, chromatography etc. These investigated mainly the ability of some adsorbent for adsorption.

The adsorption of heavy metal ions on different adsorbent have been studied extensively in order to find a specific adsorbent for each ion to be used in the treatment of wastewater in the environment . Muhammad N.et.al. (1) studied the adsorption of Pb (II), Cu (II), Cr (II) and Cd (II) onto sand. Results showed the adsorption of these heavy metals stratified the Langmuir and Freundlich isotherm. Gaikwad R.W (2) studied the removal of Cd (II) from aqueous solution by activated charcoal from coconut shell. Cadmium ion removal efficiency was enhanced by decreasing the concentration and increasing of pH of the solution pH=6 and control time of 80 minutes were found to be optimum. The study showed that (30 gm) of this adsorbent could remove the (66 %) Cd (II) from water and the adsorption conformed to the Freundlich adsorption isotherm.

Arpa, C. et.al. (3) Studied the adsorption of heavy metal ions Cu (II), Cd (II) and Pb (II) from aqueous media onto northern Anatolian smectities with a mean practical diameter of 200 µm. the adsorption rate and capacity of smectite for the selected heavy metal ions, containing different amounts of these ions (5-900 mg/L) at values ranging from pH 1.0 to 7.0 were studied. Very high adsorption rates were observed at the smectite were found to be 41.46 mg Cd(II) , 36.11 mg Pb (II) and 18.72 mg Cu(II) per gram of smectite . When the metal ions competed (in the case of adsorption from their mixture) were 11.86 mg, 11.23 mg and 16.76 mg per gram of smectite.

Al- Hamdan A.Z. and Reddy K.R. (4) studied the pH – dependent adsorption of heavy metal contamination Cr (VI), Cr (III), Ni (II) and Cd (II) by Kaolin and the sensitivity of Kaolin zeta potential to the aqueous phase. The result showed that the amount of heavy metal adsorbed by Kaolin has pronounced sensitivity to the pH. The adsorption of Cr (III), Ni (II) and Cd (II) by Kaolin increased as the pH increases. While adsorption of Cr (VI) decreased as the pH increases.

Begum S. (5) study the ability of concrete as adsorbent to adsorb silver ion from it' aqueous solution. Silver ion removal is favored by low concentration and high pH at room temperature. Gadeer .R (6) studied the adsorption of ruthenium ion on activated charcoal and the influence of temperature range of 288 K to 308 K on the kinetic of the adsorption process . It observed that the rise in temperature increases the adsorption of ruthenium ion on activated charcoal.

The Aim of Study

1- To find a suitable adsorption for treatment of pollution by this heavy metal ion from aqueous solution in the environment.
2- To know the capacity of some selected Iraqi clays (Attapulgite, bentonite, and kaolin) in removing the toxic Cobalt ion from aqueous solution by adsorption.
3- Determination the optimum conditions to adsorb higher quantity of Cobalt ion such as (temperature, pH, ionic strength, particle size, weight of adsorbent, and synergism).
4- Determination a suitable adsorption isotherm and the related constants.

1- Instruments:-

The following instruments were used throughout the work

1- Vis.Spectrophotometer / Lambed. U.S.A.
2- Thermostatic Shaker Bath. GFL (D- 3006), Fed. Rep. of Germany.
3- pH- meter ($pH_{ep)}$), HI 98107, Hanna Instruments.
4- Electric Balance, Sartorius Lab .BL 210 S, Germany. ± .0001 g.
5- Laboratory Thermal oven, Equipment LTD, Greenfield NROLDHAM.
6- Sieves of practical size (75,150 and 250 µm) of (200, 100, and 80 mesh) siever respectively.
7- Guvette – Glass.

2- Chemical compounds:-

All chemical compounds were obtainal from commercial sources and used as received.

3- Determination of Cobalt (II) as (thiocyanate) complex:-

The determination of Cobalt (II) as Co-(thiocyanate) was carried out according to the published procedure in literature (7).

4- Preparation of solutions:-

a- Standard stock solution of Cobalt (II) solution (1000 mg/ L)

A standard stock solution of cobalt (II) (1000 mg /L) was prepared by dissolving (2.390 g $CoSO_4.7\ H_2O$ in (3ml) of H_2SO_4 (conc.). The volumetric flask (500 ml) was completed to the mark with deionized water.

b- Standard stock solution of ligand (152588 mg /L)

A Standard stock solution of ligand (SCN^-) (152588 mg /L) was prepared by dissolving (50 g) of NH_4SCN in deionized water. The volumetric flask (250 mL) was completed to the mark with dionized water.

c- Cobalt (II) complex solution

Cobalt (II) complex solution was prepared in acidic medium by mixing (3 ml) of cobalt (II) solution at the desire concentration, (5 mL) of acetone (reducing the polarity water to prevent the dissociation of complex), (1 mL) of HCl conc. Finally (1 ml) of ligand (SCN$^{-)}$ solution to produce a blue complex. The volumetric flask (10 ml) was completed to the mark with deionized water.

The blank solution was prepared by mixing (3 ml) of deionized water, (5 ml) of acetone, (1 ml) of HCl (conc.) and (1 ml) of ligand (SCN^{-}) solution. The volumetric flask (10 ml) was completed to the mark with deionized water.

5- Determination of Maximum Adsorption (λ_{max}):-

Vis-scaning spectrum of (Co- thiocyanate) complex solution has been recorded as shown in figure (1). The maximum absorbance (λ_{max}) for (co- thiocyanate) was found to be at (625 nm). This value (625 nm) was utilized for measurements of quantitative estimation throughout this work.

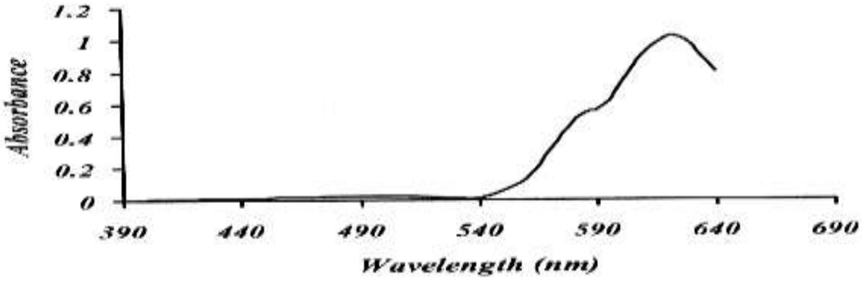


Figure (1) Spectrum of (Co –thiocyanate) complex solution shows λ_{max} at (625 nm)

6- Calibration Curve:-

(Co – thiocyanate) complex solution of different concentration were prepared as mentioned in (4 – C) by serial dilution absorbance values of these solution were measured at the specified (λ_{max}) value for (Co – thiocyanate) complex and plotted versus the concentration values as in Figure (2). These results were treated by (Least Square method). Concentration (6, 9, 12, 15, 18, 21, 24, 27, and 30 mg / L) that obey Beer- Lambert's law were then used in subsequent quantitative estimation of the concentration.

Quantities of Cobalt (II) adsorbed were determined by Visb-spectrophotometric technique.

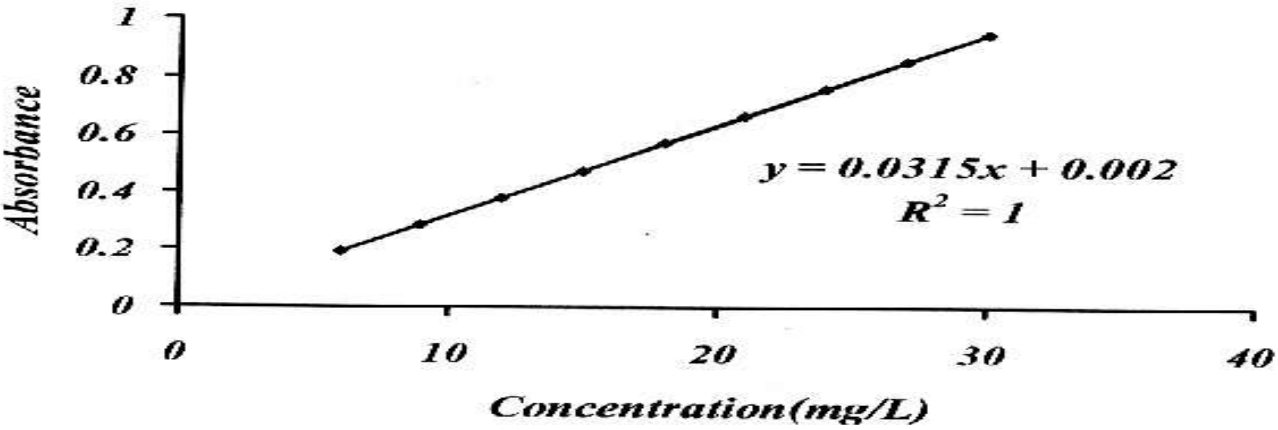


Figure (2) Calibration curve of (Co-thiocyanate) complex solution

Results and Discussion:-

1- Equilibrium times of adsorption system

The time that is sufficient for the adsorption process to reach equilibrium at 25 C° has been studied.

Table (1) shows time intervals needed for each pair adsorbent – adsorbant to attain equilibrium.

Table (1) Equilibrium time for each adsorbent – adsorbant pair

Adsorbent – adsorbant	Equilibrium time (minute)
Attapulgite – Cobalt (II)	30
Bentonite – Cobalt (II)	30
Kaolin – Cobalt (II)	15

$C_\circ$ = 30 mg /L , Particle size = 75 µm

2- Adsorption of Cobalt (II)

The adsorption of Cobalt (II) from aqueous solution on Attapulgite, bentonite and kaolin has been studied initially at the room temperature (25 C°) as well as at (10,37.5 and 50 C°) .

Table (2) shows the related results by the initial concentration of Cobalt (II) (Co) the equilibrium concentration (C_e) and the quantity adsorbed on the three clays (Q_e) .

Table (2) adsorption values of Cobalt (II) on the three clay surfaces at different temperatures.

Clays	C_o mg/L	10 C°		25C°		37.5C°		50 C°	
		C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g
Attapulgite	3	0.6317	0.1184	0.1878	0.1406	0.1295	0.3190	0.1561	0.1422
	9	4.7219	0.2139	4.0243	0.2488	3.8975	0.2551	2.2804	0.3359
	18	12.3949	0.2803	11.5705	0.3009	10.6828	0.3659	9.4462	0.4277
	27	20.0679	0.3466	19.6875	0.3545	17.4997	0.4750	16.9607	0.5019
	36	28.1533	0.3923	27.4874	0.4082	25.2996	0.5350	24.6021	0.5699
	45	36.5556	0.4222	36.0799	0.4286	34.0507	0.5475	33.2264	0.5886
	54	44.7994	0.4600	44.1652	0.4727	42.6750	0.5662	42.2945	0.5853
	63	53.4553	0.4772	52.7261	0.4963	51.1090	0.5945	50.5700	0.6215
Bentonite	3	0.1244	0.1438	0.0292	0.1485	0.1878	0.1406	0.2512	0.1374
	9	2.5341	0.3233	1.6779	0.3661	1.3292	0.3835	0.9170	0.4041
	18	8.5901	0.4705	7.6072	0.5196	7.4805	0.5259	7.2267	0.5387
	27	16.1680	0.5416	14.5193	0.6240	14.3290	0.6335	13.8852	0.6557
	36	26.2508	0.4875	25.7118	0.5144	24.9826	0.5509	24.1899	0.5905
	45	35.7946	0.4603	34.4312	0.5284	34.1776	0.5411	33.7019	0.5649
	54	42.2414	0.5789	42.1359	0.5932	41.8189	0.6091	41.3116	0.6344
	63	52.2505	0.5375	51.5529	0.5724	51.2359	0.5882	50.6651	0.6167
Kaolin	3	1.3609	0.0819	1.3609	0.0819	1.5195	0.0740	1.8365	0.0582
	9	9.9730	0.1013	7.2901	0.0855	7.4804	0.0759	7.8608	0.0569
	18	15.2168	0.1392	15.6290	0.1185	15.7242	0.1138	16.1363	0.0932
	27	22.2558	0.2372	22.9216	0.2039	23.6509	0.1678	24.1582	0.1421
	36	30.6898	0.2655	31.6410	0.2179	32.4337	0.1783	33.0678	0.1466
	45	38.9336	0.3033	40.0750	0.2462	41.1848	0.1908	41.8189	0.1591
	54	45.9725	0.4014	47.9701	0.3015	49.0164	0.2492	49.7456	0.2127
	63	55.0724	0.3964	57.0065	0.2997	57.7675	0.2616	58.5284	0.2236

Particle size = 75µm

The results showed an increase in adsorptive capacities of the three clays as the concentration of Cobalt (II) Increased until reaching a limited value [8, 9].

The maximum quantities adsorbed of Cobalt (II) on the three clays followed the order:

Bentonite > Attapulgite > Kaoline

3- Adsorption Isotherm

The general shapes of Cobalt (II) adsorption isotherms are shown in Figures (3),(4),(5) where the quantities adsorbed on Attapulgite , bentonite and kaolin (Q_e) are plotted as a function of equilibrium concentration (C_e) at(10,25,37.5, and 50 C^o) .

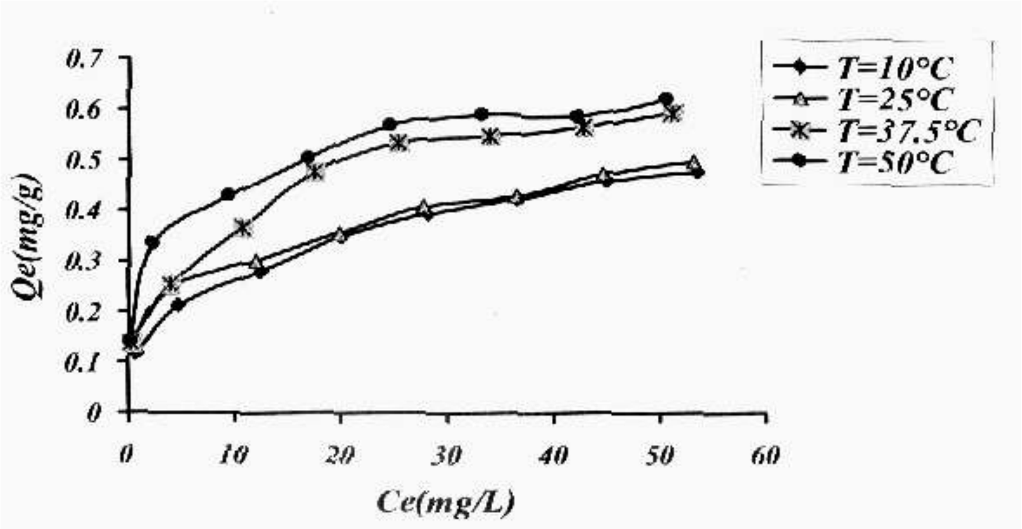


Figure (3) Adsorption isotherm of Cobalt (II) on Attapulgite surface at different temperatures.

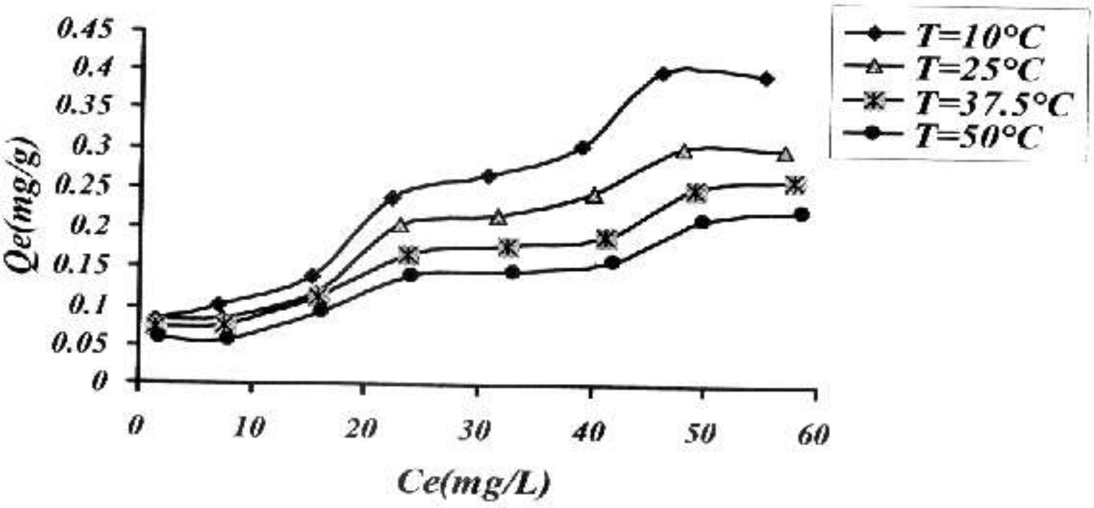


Figure (4) Adsorption isotherm of Cobalt (II) on Bentonite surface at different temperatures.

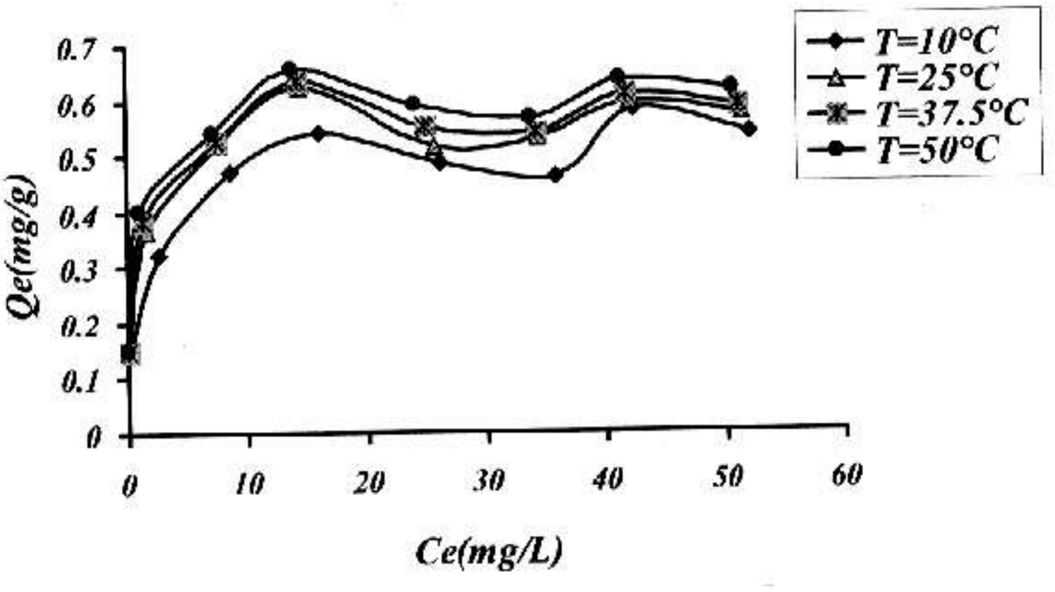


Figure (5) Adsorption isotherm of Cobalt (II) on kaolin surface at different temperatures.

The shape of the adsorption isotherm of Cobalt (II) on Attapulgite consistent with (L_3- type) on the Giles classification. The isotherm of the mentioned system obeyed Langmuire equation leading to the assumption of high adsorption affinity between the Cobalt (II) and the clay surface in addition to the formation of one adsorption layer of Cobalt (II) on the clay surface (10).

According to Giles interpretation for the adsorption isotherm shape the Cobalt (II) could be oriented indirection parallel to the surface of clay (11).

More over , the adsorption of Cobalt (II) on bentonite and kaolin was not limited to the formation of a monomolecular layer , a second rise and a second plateau was obtained , giving multilayer (L_{max} – type) and (L-type)on bentonite and kaolin of adsorption isotherm according to the classification by Giles .

This is a common observation and suggests that the surface adsorption is not in a single monolayer with single sites. Tow or three sites with different affinities and maximum may be involved in Cobalt (II) adsorption over a wide range of Cobalt (II) concentration (12).

The experimental adsorption data were applied to both the empirical Freundlich equation and the theoretical Longmuir isotherm equation. These results indicated the applicability of Longmuir isotherm as shown by the linear relationship of (C_e / Q_e) versus (C_e). Figures (6) and (7) and (8).

The result of adsorption process on kaolin surface is with a good agreement with that reported by Yayuz et al (13).

Figure (6) linear form of Langmuir isotherm of Cobalt (II) adsorbed on Attapulgite surface at different temperatures.

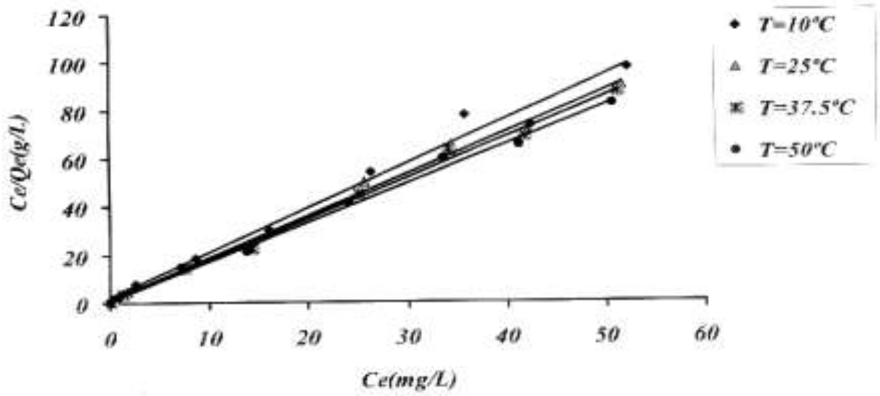


Figure (7) linear form of Langmuir isotherm of Cobalt (II) adsorbed on bentonite surface at different temperatures.

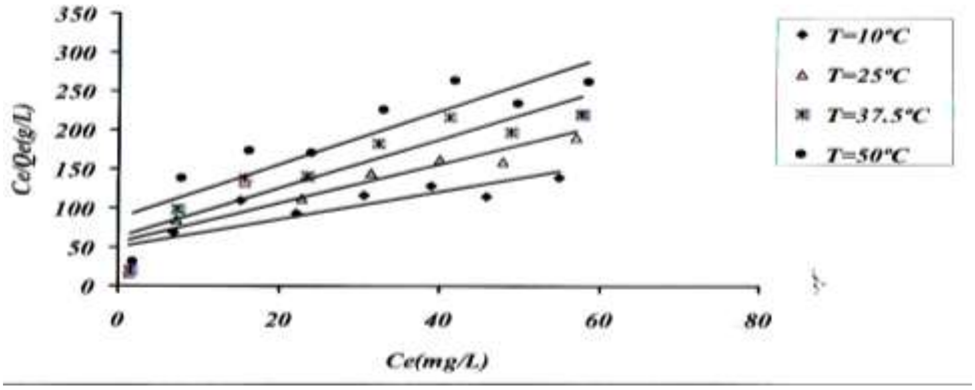


Figure (8) linear form of Langmuir isotherm of Cobalt (II) adsorbed on kaolin surface at different temperatures.

The Langmuir constant empirical values (a) (maximum adsorption capacity), (b) (energy of adsorption), and correlation coefficients of Cobalt (II) on Attapulgite , bentonite and Kaolin surfaces were abtained from the linear equation at different temperatures. The values are summarized in Table (3)

Table (3) the Langmuir constant empirical values and the correlation coefficients for the adsorption of Cobalt (II) on the three clay surfaces at different temperature.

Clays	Temperature (C^o)	a mg/g	b L/g	R
Attapulgite	10	0.5198	0.1386	0.9887
	25	0.5171	0.1821	0.9867
	37.5	0.6334	0.2072	0.9938
	50	0.6352	0.3666	0.9968
Bentonite	10	0.5443	0.7132	0.9909
	25	0.5741	1.4756	0.9964
	37.5	0.5897	1.8796	0.9972
	50	0.6195	1.5173	0.9973
Kaolin	10	0.5675	0.0348	0.8518
	25	0.4000	0.0451	0.9039
	37.5	0.3209	0.0448	0.9214
	50	0.2907	0.0396	0.8964

The results showed that ,the maximum adsorption capacity (a) of Cobalt(II) on Attapulgite and bentonite increased with an increase in temperature ,showing that (a) enhanced at higher temperatures, while the reverse effect of maximum adsorption capacity (a) was observed on kaolin surface ,which it means ,that (a) enhanced at lower temperatures (14) .

The energy of adsorption (b) is enhanced at higher temperatures on Attapulgite, and bentonite because it increased with an increase in temperatures, while it enhanced at (10 and 25 C^o) more than (37.5 and 50 C^o) on kaolin surface.

4- Effect of temperature on adsorption

The effect of temperature on the adsorption extent of Cobalt (II) on three clays (Attapulgite, bentonite, and kaolin) has been studied. Table (2) and Figures (3), (4) and (5) illustrate data and general shapes of Cobalt (II) adsorption at (10, 25, 37.5, and 50 C˚).

The results showed an increase in the amount of Cobalt (II) adsorbed on Attapulgite and bentonite with increasing temperature, hence the adsorption process appeared endothermic (15). This means the interaction between the clays (Attapulgite, bentonite) and the Cobalt (II), requires an appreciable energy in order to take place.

Endothermic Cobalt (II) uptake may also be interpreted as a consequence of possible absorption process, in which the ions diffuse inside the crystal lattice of the clay and the diffusing speed increase with increasing of temperature. This behavior attributed to absorption process, which means that absorption process may occur accompanied with adsorption process (16).

On the other hand, the adsorption extent of Cobalt (II) on kaolin was decreased with increasing temperature; suggesting an exothermic adsorption process to take places the surface (17). This means, the low temperature are the favorite for adsorption of Cobalt (II) onto kaolin. The thickness of the boundary layer decrease with the rise in solution temperature, due to the increased tendency of Cobalt (II) to escape from the solid phase to the liquid phase, and thus, as a result of an increase in kinetic energy of the adsorbant species at high temperatures ,a decrease in adsorption was observed (12) .

It can also explain the increase in the amount of Cobalt(II) adsorbed on attapulgite and bentonite with increasing temperatures according to the effect of temperature on the weak bonds between the clay platelets .Attapulgite and bentonite are consist of three platelets of aluminium –silicate connect to one another by weak bonds ,so the increase in the temperature may be broken these weak bonds that lead to change the pores geometry of the clay ,causing an increase in adsorption extent as a result of an increase in surface area of the clay .

On the other hand, kaolin is clay consists of two aluminium- silicate platelets connect to one another by stronger bonds than in attapulgite and bentonite ,so the increase in temperature will not lead to affecting increase in the surface area of kaolin clay .The increase in the quantity pf Cobalt(II) adsorbed on kaolin surface may be due to the increase in the desorption process with increasing the temperature (18) .

The study of the temperature effect on adsorption of Cobalt (II) on (Attapulgite, bentonite, and kaolin), Will help in evaluating the basic thermodynamic function Free energy (ΔG), Enthalpy (ΔH), and Entropy (ΔS) of the adsorption process.

The change in free energy (ΔG^o) could be determined from the equation (19):

$$\Delta G^o = -RT\ln K \text{ -- } (1)$$

Where
ΔG^o : is standard free energy of change ($K.J.mole^{-1}$).
R: is the gas constant ($8.314\ J.mol^{-1}.deg^{-1}$).
K: is the thermodynamic equilibrium constant.

The thermodynamic equilibrium constant (K) for the adsorption process at each temperature was calculated from the equation (20).

$$K = \frac{Xm \times 0.25g}{Ce \times 0.0125L} \text{ --- } (2)$$

Where:
Xm: is the maximum uptake of adsorption at a certain value of the equilibrium concentration (Ce) that was taken identical for all temperatures of study (mg of adsorbate per gram).
Ce: is the equilibrium concentration of the adsorbate expressed in (mg) per one liter of solution
(0.25 g): represents the weight of clay that has been used.
(0.0125 L): represents the volume of Cobalt ion solution used I the adsorption process.

The heat of adsorption (ΔH^o) may be obtained from the equation (21)

$$\ln K = \frac{-\Delta H}{RT} + cons\tan t \text{ --- } (3)$$

Table (4) gives K values at different temperatures plotting (lnK) versus (1/T) should produce a straight line with a slop = ($-\Delta H/R$) as shown in Figures (9).

The change in entropies (ΔS^o) was calculated from Gibbs equation:

$\Delta G^o = \Delta H^o - T\Delta S^o$ -- (4)

Table (4) effect of temperature on the thermodynamic equilibrium constant for adsorption of Cobalt (II) on the three clay surfaces.

T C^o	T K	1000/T K^{-1}	Attapulgite			Bentonite			Kaolin		
			C_e=11.5 mg/L			C_e=25.5 mg/L			C_e=48 mg/L		
			X_m mg/g	K	lnK	X_m mg/g	K	lnK	X_m mg/g	K	lnK
10	283	3.5336	0.27	0.4696	-0.7559	0.49	0.3843	-0.9563	0.41	0.1708	-1.7673
25	298	3.3557	0.30	0.5217	-0.6507	0.52	0.4078	-0.8969	0.30	0.1250	-2.0794
37.5	310.5	3.2206	0.38	0.6609	-0.4142	0.55	0.4314	-0.8407	0.25	0.1042	-2.2614
50	323	3.0959	0.45	0.7826	-0.2451	0.585	0.4588	-0.7791	0.20	0.0833	-2.4853

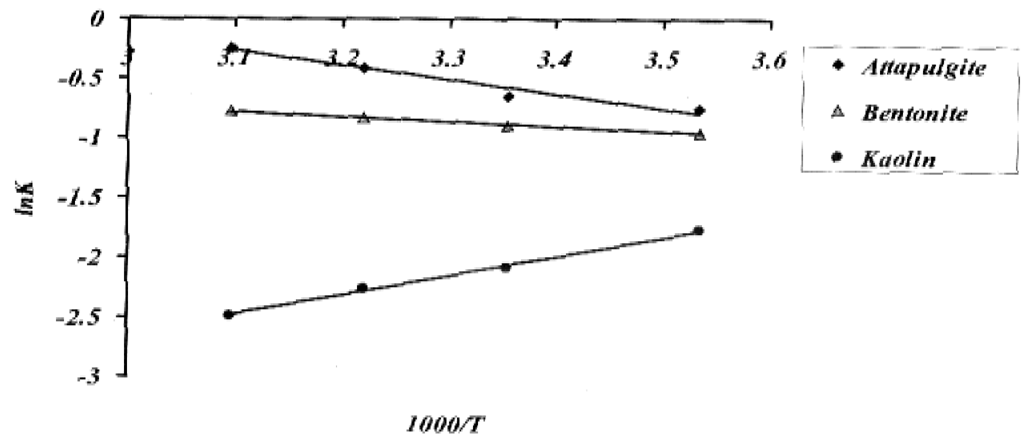


Figure (9) plot of lnK against reciprocal absolute temperature for adsorption of Cobalt(II) on the three clay surfaces .

Table (5) values of thermodynamic function for the adsorption of Cobalt(II) on the three clay surface at different temperatures

T C^o	Attapulgite			Bentonite			Kaolin		
	ΔG^o KJ.Mole^{-1}	ΔH^o KJ.Mole^{-1}	ΔS^o J.Mole^{-1}.K^{-1}	ΔG^o KJ.Mole^{-1}	ΔH^o KJ.Mole^{-1}	ΔS^o J.Mole^{-1}.K^{-1}	ΔG^o KJ.Mole^{-1}	ΔH^o KJ.Mole^{-1}	ΔS^o J..Mole^{-1}.K^{-1}
10	1.7785	+0.0099	-6.2495	2.2501	+0.0033	-7.9392	4.1581	-0.0134	-14.740
25	1.6122		-5.3768	2.2221		-7.4456	5.1519		-17.3332
37.5	1.0691		-3.4113	2.1703		-6.9791	5.8379		-18.8448
50	0.6583		-2.0074	2.0923		-6.4675	6.6741		-20.7043

Table (5) shows the basic thermodynamic values of Cobalt (II) adsorption on three clays at different temperatures.

The enthalpy values of adsorption (ΔH^o) of [Cobalt (II) –attapulgite] and [Cobalt (II) –bentonite] system were found to posses positive values indicating endothermic adsorption process (15).

On the other hand the enthalpy of adsorption (ΔH^o) of the [Cobalt (II) – kaolin] system was found to posses negative value indicating exothermic adsorption process.

The function (ΔS^o) of Cobalt (II) adsorption on three clay surfaces was found to posses negative values. This result could be viewed through the fact, that the entropy change (ΔS^o) of the ordered constrained adsorbed layer is always less than that of dissolved solutes.The thermodynamic function (ΔG^o) values of Cobalt (II) adsorption on three clays surfaces were found to posses positive values indicating non spontaneous adsorption process because the equilibrium constant are less than one (21). The decrease in (ΔG^o) values of [Cobalt (II) –attapulgite] and [Cobalt (II) –bentonite] system reveals that, adsorption of Cobalt (II) on Attapulgite and bentonite become better at higher temperature (22) .

On the other hand, the increase in (ΔG^o) values of [Cobalt (II) – Kaolin] system with increasing temperature indicates that, the non spontaneity decrease with rise temperature. This can be explained according to the negative value of enthalpy ,which is probably due to the decrease in physical forces responsible for adsorption .This behavior shows that enhanced desorption taking place resulting in total decrease in adsorption (19) .

5- Effect of Ionic Strength

The effect of ionic strength on adsorption uptake of Cobalt(II) on three clay surfaces (Attapulgite ,bentonite ,and kaolin) has been studied at variable concentration of sodium chloride (0.0009 ,0.0015, and 0.003 F) [ionic strength (I) = 0.0009 ,0.0015 , and 0.003 M] .

Table (6) and Figures (10), (11), and (12) show the influence of ionic strength on the amounts of Cobalt (II) adsorbed by Attapulgite, bentonite, and kaolin at 25C^o

Table (6) Adsorption value of Cobalt (II) on the three clay surfaces at 25 C^o from solution of different concentration of Sodium chloride

Clays	C_o mg/L	Without salt		0.0009M of NaCl		0.0015 M of NaCl		0.003 M of NaCl	
		C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g
Attapulgite	3	0.1878	0.1406	0.1878	0.1406	0.1244	0.1438	0.0609	0.1469
	9	4.0243	0.2488	4.0243	0.2488	4.3516	0.2234	4.3731	0.2313
	18	11.9827	0.3009	11.5705	0.3215	11.0315	0.3484	10.7779	0.3611
	27	19.9095	0.3545	19.6875	0.3656	19.2753	0.3862	18.9583	0.4021
	36	27.8362	0.4082	27.4874	0.4256	27.2020	0.4399	26.9801	0.4509
	45	36.4287	0.4286	36.0799	0.4460	35.4458	0.4777	35.0654	0.4967
	54	44.5457	0.4727	44.1652	0.4917	43.5628	0.5219	42.9604	0.5519
	63	53.0749	0.4963	52.7261	0.5137	52.3456	0.5327	52.0602	0.5469
Bentonite	3	0.0292	0.1485	0.1561	0.1422	0.1878	0.1406	0.2512	0.1374
	9	1.6779	0.3661	2.1536	0.3423	2.5024	0.3249	2.8194	0.3090
	18	7.6072	0.5196	8.1146	0.4943	8.5901	0.4705	8.8755	0.4562
	27	14.5193	0.6240	15.4399	0.5781	15.8827	0.5559	16.1680	0.5416
	36	25.7118	0.5144	26.6630	0.4668	27.1069	0.4447	27.4239	0.4288
	45	34.4312	0.5284	35.3824	0.4809	35.6044	0.4698	35.9531	0.4523
	54	42.1359	0.5932	42.9287	0.5536	43.3091	0.5345	43.5311	0.5234
	63	51.5529	0.5724	52.5041	0.5248	52.8212	0.5089	53.1699	0.4915
Kaolin	3	1.3609	0.0819	2.2487	0.0376	2.5341	0.0233	2.7243	0.0138
	9	7.2901	0.0855	7.9877	0.0506	8.3682	0.0316	8.6535	0.0173
	18	15.6290	0.1185	16.4851	0.0757	16.8973	0.0551	17.2461	0.0377
	27	22.9216	0.2039	24.6655	0.1167	24.9826	0.1009	25.2996	0.0850
	36	31.6410	0.2179	34.0190	0.0990	34.1459	0.0927	34.4312	0.0784
	45	40.0750	0.2462	42.9287	0.1036	43.3726	0.0814	43.6896	0.0655
	54	47.9701	0.3015	51.2359	0.1382	51.9334	0.1033	52.4090	0.0795
	63	57.0065	0.2997	60.3992	0.1300	61.0016	0.0999	61.5723	0.0714

Particle size = 75 µ

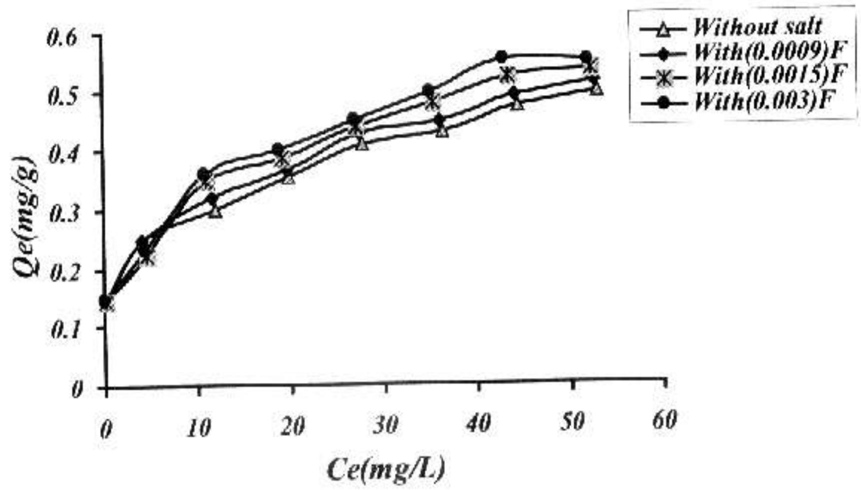


Figure (10) Adsorption isotherm of Cobalt (II) on Attapulgite in the presence of different concentration of (NaCl) at 25 C^o

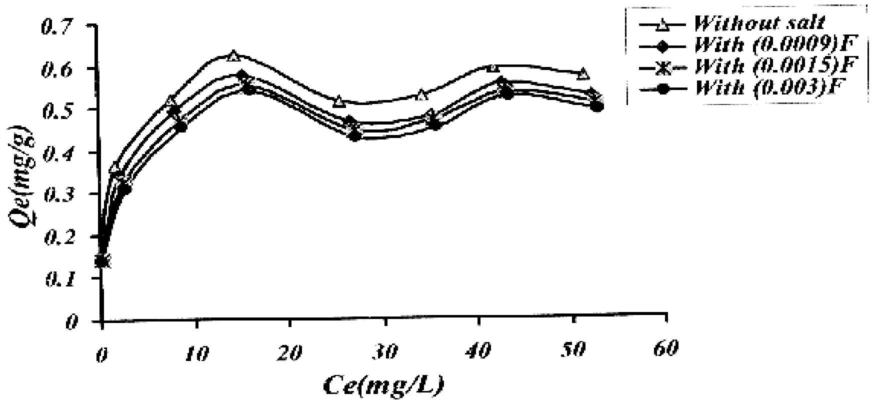


Figure (11) Adsorption isotherm of Cobalt (II) on bentonite in the presence of different concentration of (NaCl) at 25 C^o

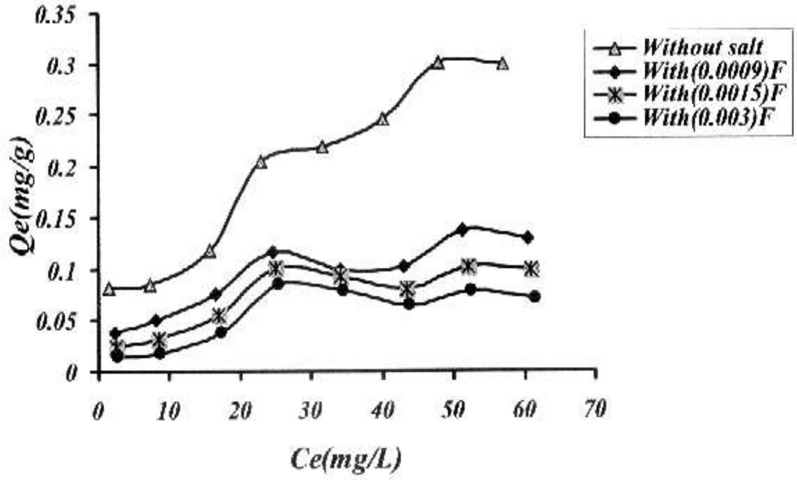


Figure (12) Adsorption isotherm of Cobalt (II) on kaolin in the presence of different concentration of (NaCl) at 25 C^o

The results showed an increase in the amount of Cobalt (II) adsorbed on Attapulgite with increasing electrolyte concentration (and hence the ionic strength).The effects of ionic strength on Cobalt (II) adsorption onto Attapulgite are two-fold. Based on the Gouy – Chapman theory, when solid phase and liquid phase are in contact, they are bound to be surrounded by an electrical diffuse double layer. The thickness of the double layer can be compressed by the presence of NaCl. The increase in adsorption with an increase in ionic strength may be due to the compression of the thickness of diffuse double layer. Such compression helps the clay particle and Cobalt (II) to approach each other more closely .These results showed that, electrostatic attraction plays a significant role in the removal of Cobalt (II) by Attapulgite. The second case depends on the solubility of Cobalt (II) in the presence of NaCl (12) .The solubility of ionic salt (NaCl) in aqueous media is normally higher than that of adsorbate as a result of higher interaction of electrolyte ions (Na^+) and (Cl^-) with the aqueous solvent than that of Cobalt (II) (23) .

Therefore, a competition between them to interact with the solvent molecules lead to increase in the attraction between the clay surface and the Cobalt (II) .

On the other hand, the adsorption extent of Cobalt (II) has decreased on bentonite and kaolin in the presence of electrolyte. These results may be due to the competition between the Cobalt (II) and the electrolyte ions on the active site of the surface, so the adsorption will decrease as a result of reducing the electrostatic attraction between the Cobalt (II) and the surface clay (24). Moreover , bentonite surface has the ionic – exchange characteristic with other species of ions. This characteristic depends on the size, valence, and stereo orientation of ions toward the surface. That is meaning that the ions of the additive electrolyte (Na^+) and (Cl^-) would adsorb preferentially on the particles of adsorbent (25).

It found that the relationship between the ionic strength (I) and the adsorption quantity (Q_e) at a fixed equilibrium concentration is a linear relationship as illustrate in Table (7) and Figure (13).

Table (7) the relationship between the ionic strength and the adsorption quantity of Cobalt(II) on the three clay surface at 25 C^o .

Attapulgite		Bentonite		Kaolin	
C_e =19.5 (mg /L)		C_e =35.5 (mg /L)		C_e =34 (mg /L)	
I	Q_e	I	Q_e	I	Q_e
0.0009	0.36	0.0009	0.48	0.0009	0.1
0.0015	0.385	0.0015	0.47	0.0015	0.09
0.003	0.415	0.003	0.45	0.003	0.08

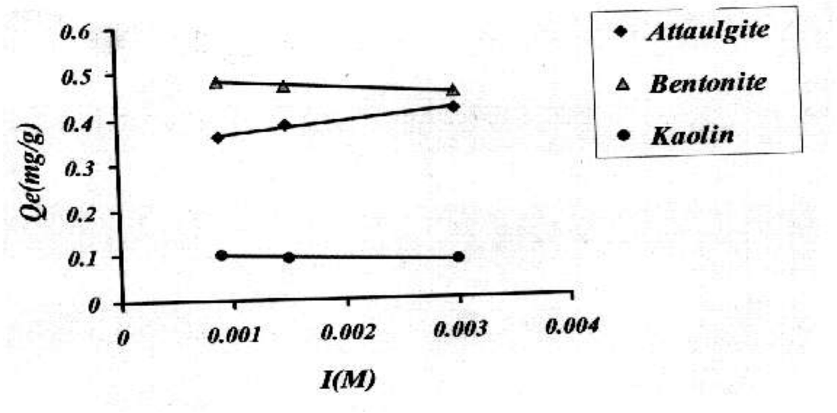


Figure (13) the relationship between the ionic strength and the adsorption quantity of Cobalt(II) on the three clay surface at 25 C^o

Depending on the linear relationship between (I) and (Qe) ,Figure (13) , it proposed the following empirical equation between (I) and(Qe) :

Q_e=Q_e^o –AI --(5)

Where Qeo : the adsorption Quantity at [I=zero] .
A: Empirical constant for the system (28) .

According to the slop and straight –line intercept for linear relationship between (I) and (Qe) ,the equations of Cobalt(II) with the three clays are illustrated in Table(8).

Table (8) the equations of Cobalt(II) on the clay surfaces at 25C^o according to the linear relation ship between (I) and (Qe) .

Clays	The Equation	R^2
Attapulgite	Qe=0.3417 -25 I	0.9643
Bentonite	Qe=0.4921 +14.103 I	0.9973
Kaolin	Qe=0.1062 +8.9744 I	0.9432

6- Effect of pH on the adsorption

The effect of pH on the adsorption of Cobalt (II) with the three clays (Attapulgite, bentonite, and kaolin) in different media (pH =2, 4, and 6) has been studied using a fixed concentration at 25 C^o . Figure (14) demonstrate the influence of pH on the adsorption.

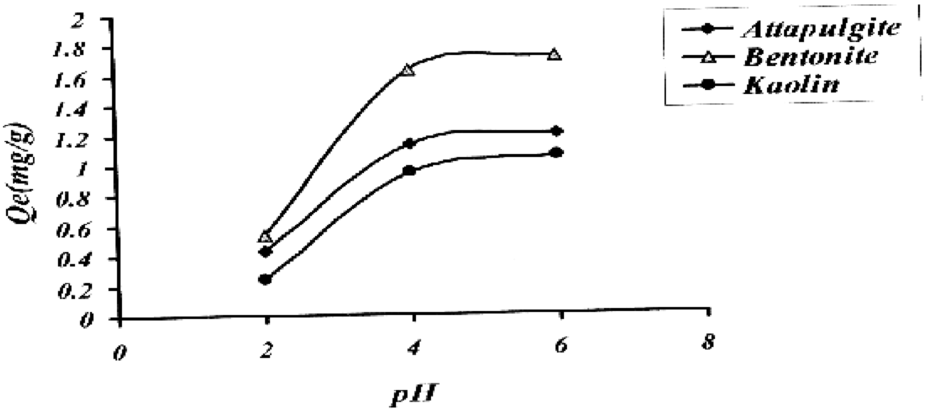


Figure (14)
Effect of pH on adsorption of Cobalt(II) on the three clay surface at 25 C^o .

The results showed an increase in adsorption quantities of Cobalt (II) on three clay surfaces with increasing pH values of the solution.

This result may be considered in general as a consequence of the competition between solvent – surface, solvent – solute, and solute – surface interaction as the pH is varied.The changes in these interaction may be due to the change in the degree of dissociation of acidic or basic functional groups of the solute, the solvent, and the surface The in turn affects the polarization of these species and subsequently influences the adsorption extent (17) .

At low pH, a competition exerted by the hydronium ions is expected to cause a significant reduction in adsorption of Cobalt (II) .The increase in acidity of solution (decreasing pH) may increase the reaction of Al $(OH)_3$ component of the clay with sulphuric acid to produce $Al_2(SO_4)_3$ which turn influence the efficiency of the clay surface and causing a decrease in Cobalt (II) adsorption (26) .

Moreover, it was suggested that a marked increase in the adsorption of some materials onto kaolin with increasing pH value, is due to an increase in density of the negative change on the edges of kaolin particles.

In addition ,the solubility of Cobalt (II) is greatly decreased as the pH is increased from 2 to 6 causing an increase in adsorption affinity towards the clay surface .Adsorption of Cobalt (II) at higher than 6 is inapplicable because of precipitation of Cobalt ions at pH= 7 .

7- Effect of particle size

Effect of particle size on adsorption process of three the clays has been studied by using a fixed concentration and three samples of same weight of adsorbate with different particles size (75,150,and 250 µm) .

Figure (15) illustrate the influence of particle size of the adsorbent on the amount of Cobalt (II) adsorbed by attapulgite, bentonite and kaolin at 25 C^o.

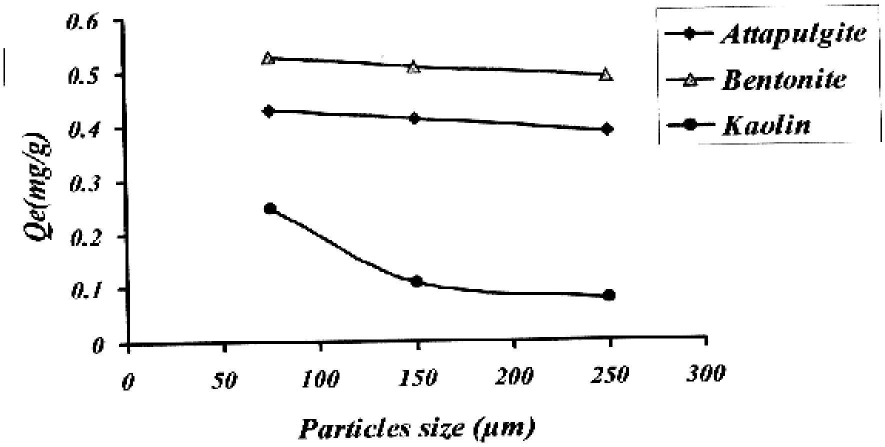
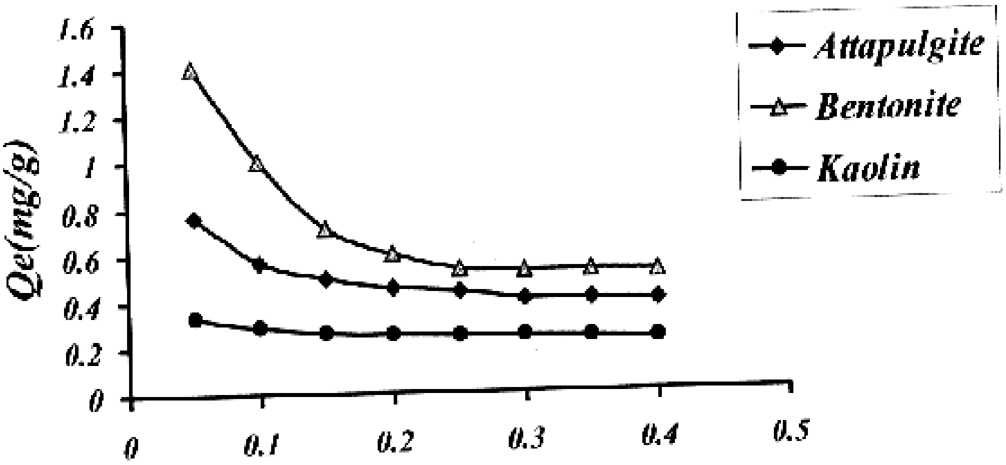


Figure (15) Effect of particles size on adsorption of cobalt (II) on the clay surfaces at 25 C^o

The results showed an increase in adsorption extent of the Cobalt (II) on the three clays with decreasing particles size .It is known that the broken of the large particles to smaller would lead to an increase in the surface area and causing an increase in Cobalt (II) adsorption $^{(27)}$.

8- Effect of Adsorbent Weight Change

Effect of adsorbent weight change on adsorption process of the three clays (attapulgite ,bentonite and kaolin) has been studied by using a fixed concentration of Cobalt (II) and different weight (0.05,0.1,0.15,0.2,0.25,0.3,0.35, and 0.4) for each clay at 25 C^o .Figure (16) demonstrate the



influence of adsorbent weight change on adsorption percentage for Cobalt (II) .

Figure (16) Effect of adsorbent weight on adsorption of Cobalt (II) at 25 Co on the three clay surfaces of different weight.

As seen in Figure (16) the curves approach the plateau region with increasing the adsorbent weight .This plateau value represents the amount of the adsorbent at saturation stage .The plateau value for attapulgite ,bentonite and kaolin were (0.2,0.25,and 0.15 g) respectively .

9- Effect of Synergism

Effect of synergism (mixing two clays with each other) has been studied by using a fixed concentration of Cobalt (II) at 25 C^o .

Table (9) demonstrates the influence of synergism on adsorption process.

Table (9) adsorption values of Cobalt (II) from solution at 25Co by different adsorbents .

Adsorption	Ce mg/L	Qe mg/g
Attapulgite	36.4287	0.4286
Bentonite	34.4312	0.5284
Kaolin	40.0750	0.2462
Attapulgite+Bentonite	34.3678	0.5316
Kaolin +Attapulgite	37.2848	0.3858
Kaolin + + Bentonite	36.5556	0.4222

*Co=45mg/L, particle size = 75µm.

The results showed that the mixing of attapulgite with bentonite (as adsorbent) , enhanced the adsorption process of Cobalt (II) on both attapulgite and bentonite . On the other hand, the mixing process of kaolin with attapulgite and bentonite, enhanced the adsorption process of Cobalt (II) on kaolin, but reduce the adsorbate amount on both attapulgite and bentonite.

This result may be due to the (Imbibition process) which observed clearly in both attapulgite and bentonite .This process lead to swell the clay and it is greatly clear in dilute solution. The continuance swelling to reduce the osmotic pressure between the clay platelets and the surrounding solution, weaken the bonds between these platelets and may be broken these bonds which lead to change the pores geometry of the clay, causing an increase in adsorption extent as a result of an increase in surface area of the clay . The same process may be observed in kaolin but much less than other clays (26) .

Conclusions

1- The three clays in this study (Attapulgite ,Bentonite ,and Kaolin) have a high ability for adsorbing the Cobalt ion; however ,bentonite has the highest one .

2- The sequence of the ability of these surfaces for the adsorption of Cobalt ion follows

Bentonite > Attapulgite >Kaolin

This sequence of activity of the three surfaces remained unchanged with the changing of temperature, ionic strength, pH, particles size, adsorbent weight, and synergism.

3- Adsorption isotherm of Cobalt ion on the surfaces of Attapulgite and bentonite obeyed Langmuir relation, whereas it's adsorption on kaolin obeyed Freundlich relation. These results in general indicated that the surface heterogeneity leading to different adsorption forces from site to site and different affinities toward Cobalt ion.

4- Results concerning the effect of increasing temperature on the adsorption process revealed that, there was an increase on the extent of adsorption uptake of Cobalt ion with bentonite and Attapulgite, and there was a decrease in adsorption extent of Cobalt ion with increasing of temperature with kaolin.

5- Results concerning the effect of increasing ionic strength of the solution on the adsorption of Cobalt ion indicated that there was an increase in the quantity of Cobalt ion adsorbed on Attapulgite and there was a decrease in the quantity of Cobalt ions adsorbed on bentonite and kaolin .

6- Results concerning the effect of pH on the adsorption of Cobalt ion on the different surfaces showed that ,the maximum quantities of the Cobalt ion adsorbed on the three surfaces at 25 Co followed the order :

PH =6 > pH =4 > pH = 2 .

7- The adsorption amount of Cobalt ions on the three clays increase with the decreasing particle size.

8- The adsorption percentage for Cobalt ions increase with the increasing of adsorbent weight.

9- Mixing Attapulgite with bentonite enhanced the adsorption process of Cobalt ions on both Attapulgite and bentonite ,whereas the mixing process of kaolin with Attapulgite and bentonite , enhanced the adsorption process of Cobalt ion with kaolin ,but the reverse effect has been noticed with both Attapulgite and bentonite .

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