ASTUDY THE ADSORPTION OF IRON (III0 ION ON SELECTED IRAQI CLAY SURFACES

على أسطح أطيان عراقية مختارة (III) دراسة حول امتزاز ايون الحديد

Prof .Dr.Abdul Muhsen Al-Haidary
*Ass.prof Dr.Alaa Fraq Hussain
Ruaa Moayed Mahmmod
Department of chemistry –college of Education –Ibn Al-Haitham , University of Baghdad
* Department of chemistry –college of Science ,University of Karbala
أ.د. عبد المحسن عبد الحميد الحيدري
أ.م.د علاء فراك حسين *
رؤى مؤيد محمود العاني
قسم الكيمياء –كلية التربية /ابن الهيثم – جامعة بغداد
قسم الكيمياء –كلية العلوم –جامعة كربلاء

Abstract :

This work is concerned with one of application of adsorption from solution .It deals with the study of the ability of selected clay surfaces (Attapulgite , Bentonite and Kaoline) for the adsorption of iron(III) ion . The target of study is to search for suitable surfaces which posses high activity for the adsorption of iron (III) ion ,and the to use these surfaces for treatment of the pollution of aqueous solution by this heavy metal ion.The technique of Vis- spectrophotometry has been utilized for the determination of the quantity of ion adsorbed by forming a colored complex with NH_4SCN (Ammonium thiocyanate) , construct the relation between the amount of the adsorbate (ion) and the concentration of equilibrium leads to know the adsorption isotherm in different condition of pH ,temperature ,ionic strength ,particles size and adsorbent weight .

الخلاصة :

يتناول هذا البحث احد تطبيقات ظاهرة الامتزاز من المحلول حيث تم دراسة قابلية أسطح أطيان عراقية مختارة (الاتابلكايت ,البنتونايت , والكاؤلين) لامتزاز ايون الحديد الثلاثي .لغرض البحث عن أسطح مناسبة تمتلك فعالية عالية لامتزاز ايون لحديد (III) , ومن ثم استعمال هذه السطوح لمعالجة تلوث المحاليل المائية بايون هذا العنصر الثقيل ومستقبلا لعناصر ذات سمية عالية. تم استخدام تقنية الأشعة المرئية لتعيين كمية الايون الممتز عن طريق تكوين معقد ملون مع الكاشف NH_4SCN (ثايوسيانات الامونيوم) , من رسم العلاقة بين كمية الممتز (الايون) والتركيز عند الاتزان تم التعرف على ايزوثرم الامتزاز في ظروف مختلفة من pH ,درجة الحرارة ,الشدة الأيونية ,حجم الدقائق ووزن السطح الماز .

Introduction :

There are many studies of adsorption in different fields such as ,medicine ,pollution , chromatography and other fields . These studies investigate manly the ability of some adsorbents for adsorption. The search for a new ,available ,cheap and save adsorbent in the treatment of pollution is still a good field for study .

Qadeer [1] studied the kinetics of the adsorption of lead ions on active carbon from aqueous solution at room temperature ,and found the active carbon is a good adsorbent for lead ions ,and the kinetics of the adsorption were rapid in the initial stage followed by a slow rate .

Gardea [2] studied the adsorption of toxic heavy metals such as Pb(II) ,Cd(II) ,Ni(II) ,Cr(II) and Cr(VI) a well as some elements for Lanthanide and actinides groups from contaminated aqueous solution by using different agricultural biomasses .

Bektas [3] studied the competitive adsorption of the heavy metal ions Cu(II) , Cd(II) and Pb(II) from aqueous media onto northern Anatolian smectites with a mean particle diameter o 200 µm , and found the order of affinity based on weight uptake by smectite was Cd(II) >Pb(II) >Cu(II) .

Qadeer [4] studied the influence of temperature on ruthenium adsorption on activated charcoal in the range 288K to 308K . It was absorved that the rise in temperature increases the adsorption of ruthenuium ions on activated charcoal and follows the kinetics of first order rate law with rate constant value (0.0564 – 0.0640 min -1) at the temperature range of 288K to 308K respectively .

Zhou [5] studied the adsorption characteristics of heavy metal ions onto suspended particles and bottom sediments of the Weiho and Hanjiang rivers in china .

Adsorbents are suspended particles and bottom sediments of typical section of these two rivers .Adsorbates are four heavy metal ions Cd,Zn,Cu and Pb . Salim [6] has studied the effects of the chemical composition and particle size of suspended in river water on the adsorption of lead onto these particles . Xiaoyuon[7] has studied adsorption of heavy metal ions Cu,Zn and Ni onto sediments in the Jionshajing river , and the results showed that the Ph of river water is an important factor for adsorption heavy metal ions onto sediment .

The aim of this study is to investigate the removal of toxic heavy metal Fe(III) from aqueous solution by adsorption onto three locally available clays (attapulgite , bentonite and kaolin) to determine the ability of three clays in the adsorption of Fe(III) from solution ,and to determine the optimum removal condition and the suitable adsorption isotherms . The expected adsorptive activity of these clays toward the ion may give an indication for using them as materials in the treatment of pollution due to other heavy metal ions .

Experimented

1- Instruments

The following instruments were used throughout the work :-

1) Vis spectrophotometer /Lambed . Inc. U.S.A .
2) Thermo stated Shaker Bath ,GFL (D-3006),Fed.Rep. of Germany .
3) pH-meter (pHeq),HI 98107 ,Hanna Instruments .
4) Electronic Balance ,Sartoriue Lab. BL 210 S,Germany ,±0.0001 g.
5) Sieves of particle size (75,150 and 250 µm) of (200,100 and 80 – mesh)sieve respectively .
6) Laboratory thermal Oven ,Equipment LTD, Green field .NROLDHAM .
7) Cuvette –Glass .

2- Chemicals

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

3- Preparation of clay powders

The clays of attapulgite ,bentonite and kaoline were supplied in powder form .They were washed with excessive amounts of deionized water several times to remove the soluble materials .Washed clays were dried in an Oven at ($150C^0$) for (3 hours) , left to cool at room temperature and then kept in airtight constrainers. The clays were ground using a mill and sieved by the available sieves to obtain a particles size of (75,150,250 µm) by using a (200,100,80 – mesh) sieves respectively .

The particle size of (75 µm) was used for the three clays in all experiments of this work , while other particles size were used for particle size study .

4- Preparation of Solutions .

a.The standard stock solution of Iron (III) (2000 mg/L)

The standard stock solution of Fe(III) (2000 mg /L) was prepared by dissolving (2.9045 g) of $FeCl_3$ anhydrous in sufficient deionized water , added (5 ml) of HNO3 (10 M) and then completed the volume with deionized water in volumetric flask to (500 ml) .

b.The standard stock solution of Ligand (152588 mg/L)

The standard stock solution of SCN- (152588 mg/L)was prepared by dissolving (50g) of Ammonium thiocyanate in deionized water and completed the volume to the mark volumetric flask (250 ml) .

5- Determination of Iron (III)

The determination of Fe (III) ion was carried out according to the procedure in literature [8] . Fe (III) is complexed with SCN- to yield colored complex $[Fe(SCN)n]_{3-n}$. This complex was prepared in acidic medium by mixing (5 ml) of Fe (III) solution at the desire concentration , (1.5 ml) of HNO_3 (10 M) and (1 ml) of SCN^- solution at concentration (152588 mg/L) and then completed the volume with deionized water in volumetric flask to (10 ml) . The red color of the complex is then measured spectrophotometrically at (λ_{max}) of the complex .

6- Determination of Maximum Absorption ; λ_{max}

Visible scanning spectrum of Fe (III) complex has been recorded as shown in Figure (1) . Wave length value corresponding to the maximum absorbance (λ_{max}) for Fe (III) complex was found to be (480 nm) . This value was utilized for the measurements of quantitative estimations throughout this research .

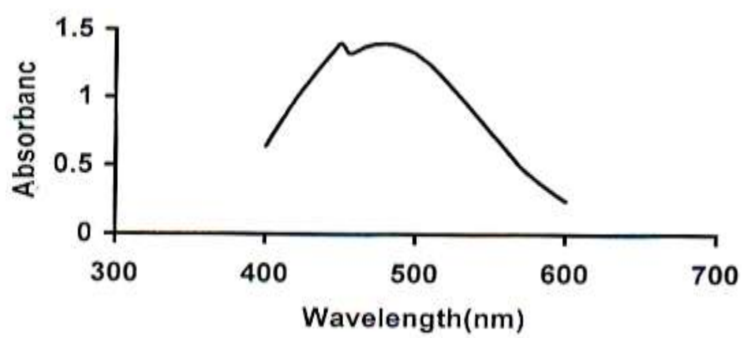
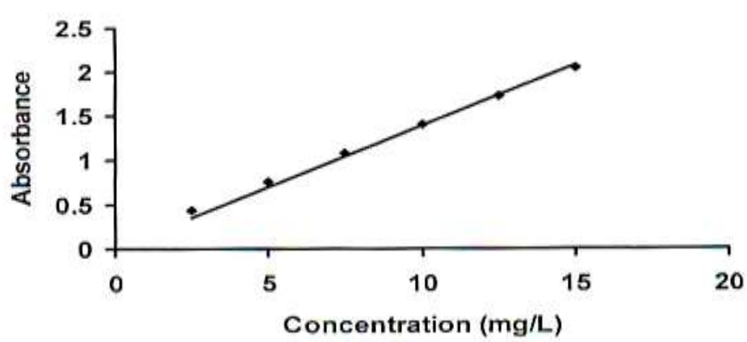


Figure (1): Visible spectrum of the Fe(III) complex

7- Calibration Curve

Different concentration of Fe(III) complex solution were prepared by serial dilution of the stock solution .Absorbance values of these solutions were measured at the specified (λ_{max}) value (480 nm) and plotted versus the concentration values . These results were treated by (Least Square Method) as shown in Figure (2) . The concentration range till (15 mg/L) that falls in the region of applicability of Beer- Lambert 's Law which then used in subsequent quantitative estimation .



Figure(2) :Calibration curve of the Fe(III) complex Y=0.1388X , r=0.9964

Results and Discussion :

1- The Equilibrium Times of Adsorption Systems

The time that is sufficient for the adsorption to reach equilibrium was determined by using a fixed concentration of Fe(III) ion at 25 C^0 . The equilibrium times of adsorption Fe (III) ion on the three clays are shown in Table (1)

Table (1) :Equilibrium times for each adsorbent –adsorbate pair .

C^0 (mg/L)	Adsorbent–Adsorbate pair	Equilibrium time (minute)
800	Attapulgite – Iron (III)	45
50	Bentonite – Iron (III)	15
10	Kaolin – Iron (III)	30

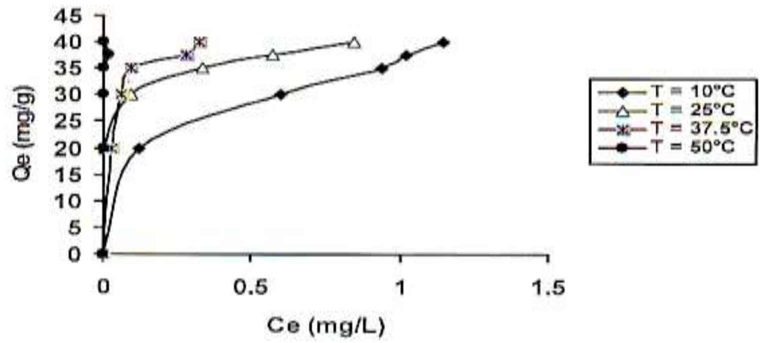
2- The Adsorption Isotherm of Fe(III) Ion

The adsorption of Fe (III) ion from aqueous solution on attapulgite ,bentonite and kaolin has been studied initially at the room temperature (25 C^0) then at other three temperature (10 ,37.5 and 50 C^0) as indicated in Table (2) , where , (C_0) represent the initial concentration of Fe(III) , (C_0) the equilibrium concentration and (Cle) the quantity adsorbed on the three clay .
The quantity adsorbed (x/m or Q_e) has plotted versus equilibrium concentration to obtain the general shape of the adsorption isotherm as shown in Figures (3),(4) ,(5) which represent the isotherms of Fe (III) ion on three clays at different temperatures .

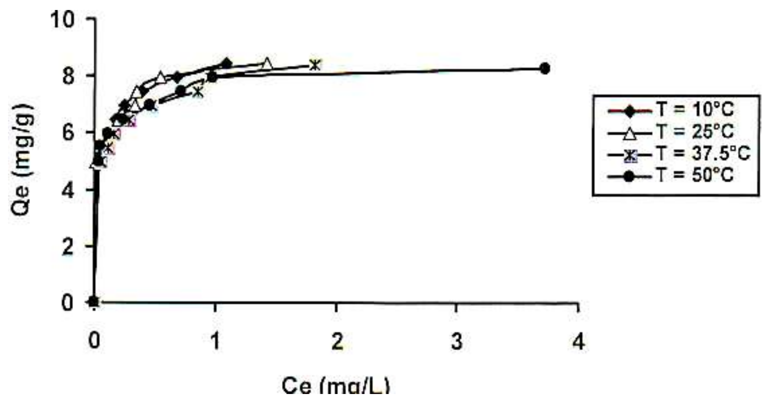
Table (2) : Adsorption values of Fe (III) ion on the three clays at different temperatures .

Clays	C_0 mg/L	10 C^0		25 C^0		37.5 C^0		50 C^0	
		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	400	0.1225	19.9939	0.0072	19.9996	0.0288	19.9986	0.0000	20.0000
	600	0.5980	29.9701	0.0937	29.9953	0.0576	29.9971	0.0000	30.0000
	700	0.9366	34.9532	0.3314	34.9834	0.0937	34.9953	0.0000	35.0000
	750	1.0159	37.4492	0.5692	37.4715	0.2810	37.4860	0.0144	37.4993
	800	1.1455	39.9427	0.8429	39.9579	0.3242	39.9838	0.0000	40.0000
Bentonite	100	0.0432	4.9978	0.0144	4.9993	0.0504	4.9975	0.0432	4.9978
	110	0.0648	5.4968	0.0504	5.4975	0.1153	5.4942	0.0504	5.4975
	120	0.1225	5.9939	0.1657	5.9917	0.1657	5.9917	0.1153	5.9942
	130	0.1729	6.4914	0.2017	6.4899	0.2882	6.4856	0.2378	6.4881
	140	0.2450	6.9878	0.3314	6.9834	0.4683	6.9766	0.4539	6.9773
	150	0.3963	7.4802	0.3458	7.4827	0.8501	7.4575	0.7205	7.4640
	160	0.6844	7.9658	0.5403	7.9730	0.9510	7.9524	0.9726	7.9514
	170	1.0951	8.4452	1.4193	8.4290	1.8156	8.4092	3.7248	8.3138
Kaolin	5	0.0720	0.2464	0.0144	0.2493	0.1585	0.2421	0.1225	0.2439
	10	0.1081	0.4946	0.1801	0.4910	0.1585	0.4921	0.1657	0.4917
	15	0.2089	0.7396	0.1945	0.7403	0.2089	0.7396	0.3602	0.7320
	20	0.7349	0.9633	0.6052	0.9697	0.6196	0.9690	0.4107	0.9795
	25	3.3285	1.0836	3.9265	1.0537	2.2046	1.1398	1.2968	1.1852
	30	5.9222	1.2039	6.5202	1.1740	3.9337	1.3033	2.1182	1.3941
	35	9.7262	1.2637	10.4464	1.2277	8.0620	1.3469	3.1844	1.5908
	40	13.0908	1.3455	13.5879	1.3206	11.9957	1.4002	4.3732	1.7813

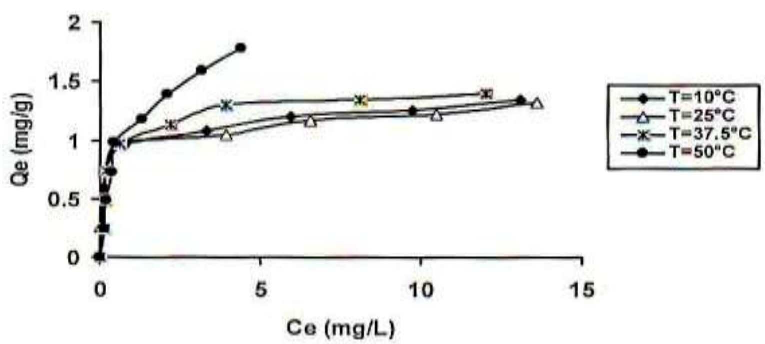
*** Partial size (75 µm)**



Figure(3) :Adsorption isotherm of Fe(III) ion on attapulgite surface at different temperatures .



Figure(4) :Adsorption isotherm of Fe(III) ion on bentonite surface at different temperatures .

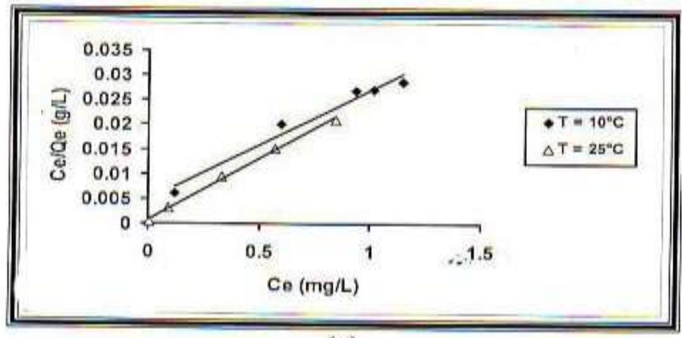


Figure(5) :Adsorption isotherm of Fe(III) ion on kaoline surface at different temperatures .

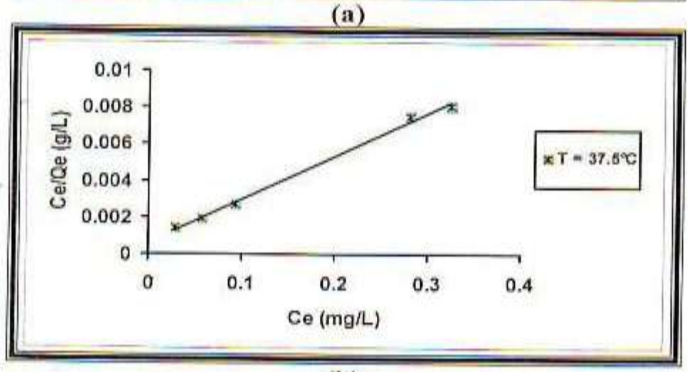
The results showed an increase in adsorptive capacities of the three clays as the concentration of Fe(III) ion increase until reaching a limited value [9] .

The general shape of the adsorption isotherm of Fe(III) ion on the three surface (attapulgite , bentonite , and kaoline) consistent with (L – type) on the Gile 's classification . The isotherm of the mentioned system obeyed Longmuir equation leading to the assumotion of high adsorption affinity between the Fe(III) ion and the three clays [10] . It is strongly adsorbed on the adsorbent , and that there is no competition from the solvent for adsorbent sites . It also indicates that the adsorption of Fe(III) ion is enhanced at higher concentrations [11] .

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 according to the values of linearity (r^2) as shown by the linear relationship of (C_e / Q_e) versus (C_e) at different temperatures Figures (6) ,(7) and (8) .



(a)



(b)

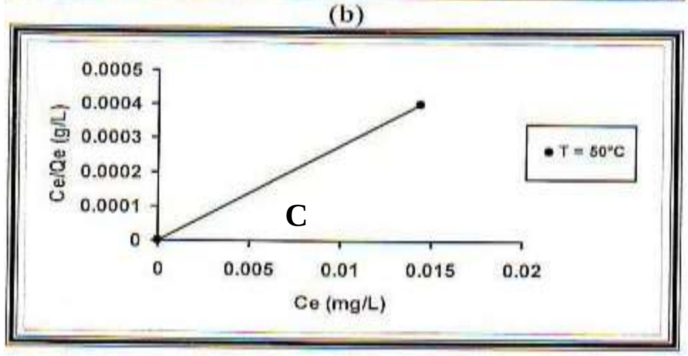


Figure (6) : Linear form of Longmuir isotherm of Fe(III) ion on attapulgite at (a) 10,20C^o,(b)37.5C^o,(c) 50C^o .

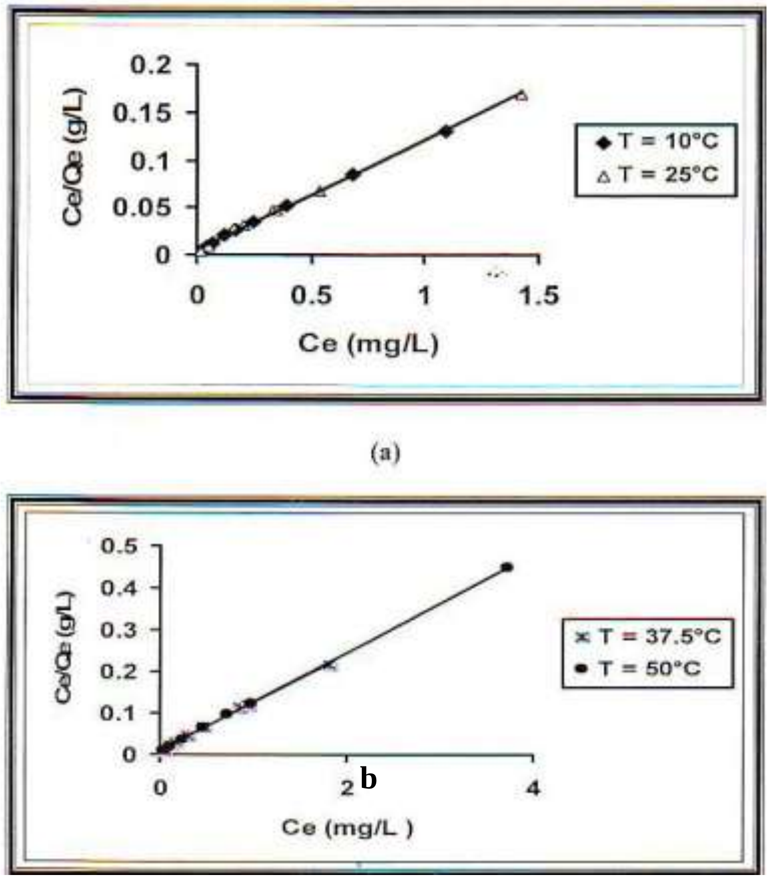


Figure (7) : Linear form of Longmuir isotherm of Fe(III) ion on bentonite at (a) 10,25 C^o,(b)37.5C^o, 50C^o .

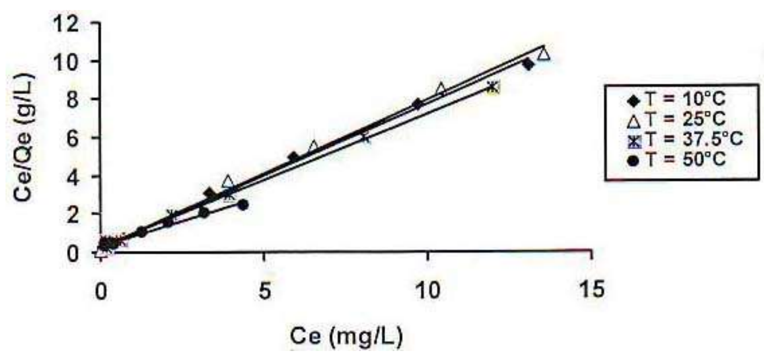


Figure (8) : Linear form of Longmuir isotherm of Fe(III) ion on kaolin at different temperature (10,25,37.5 and 50C^o) .

The values of Longmuir constants (a and b) which related to adsorption capacity and energy of adsorption or equilibrium constant respectively and the correlation coefficients of Fe(III) ion on the three surface which are obtained from the linear forms of Longmuir isotherms at different temperatures , are listed in Table (3) .

Table (3) :The Longmuir constants and correlation coefficients for the adsorption of Fe(III) ion on the three clays at different temperatures .

T (C^o)	Attapulgite			Bentonite			Kaolin		
	a	b	r	a	b	r	a	b	r
10	73.5294	1.1057	0.9845	8.7184	19.4407	0.9993	1.3428	2.6427	0.9983
25	40.4858	35.3357	0.9983	8.6655	19.8965	0.9986	1.3012	2.8891	0.9975
37.5	42.1941	39.5257	0.9985	8.6356	12.3191	0.9985	1.4401	2.2978	0.9990
50	35.9712	1391	1.0000	8.4175	17.2174	0.9998	1.9755	1.4827	0.9925

As it can be seen from the results in Table (3) , the adsorption capacity (a) decreased with an increase in temperatures on attapulgite and bentonite , showing that (a) enhanced at lower temperatures ,while the inverse effect of adsorption capacity was observed on kaolin surface , and it means that (a) enhanced at higher temperatures .

The energy of adsorption (b) is enhanced at higher temperatures on attapulgite surface because it was increased with on increase in temperatures , while it enhanced at lower temperatures on bentonite and kaoline surface (11) .

3- Effect of pH on the Adsorption

The adsorption of Fe(III) ion on the three clays (Attapulgite , Bentonite and Kaoline) have been studied at different pH .

Table (4) demonstrate the effect of pH on the adsorption uptake of a fixed ion concentration of Fe(III) by the three surface at 25 C^o .

Table (4) Values of Fe(III) ion uptake by the three clays at 25 C^o from solution of different pH values .

Attapulgite (C_o=650mg/L)			Bentonite (C_o=150mg/L)			Kaoline (C_o=28mg/L)		
pH	C_e mg/L	Q_e mg/g	pH	C_e mg/L	Q_e mg/g	pH	C_e mg/L	Q_e mg/g
1.1	0.0432	32.4978	1.5	0.3458	7.4827	2	3.4942	1.2253
1.3	0.0648	32.4968	1.9	0.3890	7.4805	7	0.9798	1.3510
1.8	0.1225	32.4939	2.3	0.1657	7.4917	11	0.5980	1.3701

As shown in Table (4) the adsorption of the Fe(III) ion on attapulgite surface decreased with increasing pH values (decreasing in acidity) , this result may be attributed to the hydronium ions which dose not play a role as a competitor (12) .

On the other hand , the adsorption of Fe(III) ion on bentonite and kaoline surfaces increased with increasing pH values .These results may be due to the possible changes in properties of the clay surface (13) .At low pH value ,binding sites are generally protonated or positively charged (by the hydronium ion) , thus repulsion occurs between the metal cation and the adsorbent .

At higher pH value , binding sites start deprotonation , making different functional groups available for metal binding . In – general , cation – binding increases as pH increases (14) .

The increase in acidity of solution may increase the reaction of $Al(OH)_3$ component of the clay with nitric acid to produce $Al(NO_3)_3$, which in turn influence the efficiency of the clay surface and causing a decrease in Fe(III) adsorption (15) .

In addition , the solubility of Fe(III) ion is greatly decreased as the pH is increased causing an increase in adsorption affinity towards the clay surface [16] .

Because of precipitation of the ion at pH ≈2,3 and 12 for attapulgite ,bentonite and kaoline respectively ,the adsorption was inapplicable at pH higher than 1.8,2.3 and 11 .

4- Effect of Temperature on Adsorption

The effect of temperature on the removal of Fe(III) ion from aqueous solution by (attapulgite , bentonite and kaoline) was studied by varying temperature between 10 and 50 C^o . Table (2) and Figures (3) ,(4) and (5) illustrate the data and the general shapes of Fe(III) ion adsorption isotherm at (10,25,37.5 and 50 C^o)

The results showed a slight effect on the extent of adsorption uptake of Fe(III) ion on the three surfaces with increasing temperature . This little effect of temperatures on adsorption reflecting a relatively strong forces binding the ion to the clay surfaces .

The slight increase in adsorption Fe(III) ion on attapulgite and kaoline can be attributed to changes that may take place on the properties of the clay surfaces leading to an increase in the sorption process ,which in turn cause an increase in adsorption uptake .The adsorption processes on attapulgite and kaoline are endothermic processes therefore ,the increase in temperature may enhance the adsorption uptake even more [17] .

The slight decrease in the adsorption extent of Fe(III) ion on bentonite surface with increasing the temperature ,suggesting an exothermic adsorption process to take place on the surface .This corresponds to a weakening of the attractive forces between the solute-solid surface and the solute – adjacent adsorbed solute with increasing temperature ,Thus ,if the ion is distributed between the adsorbed layer and the solution in a partition equilibrium , the position of the equilibrium is displaced in favor of the solution as the temperature rises .

On the other hand ,the thickness of the boundary layer decreases with the rise in solution temperature , due to the increased tendency of Fe(III) ion to escape from the solid phase to the liquid phase ,and thus ,as a result of an increase in the kinetic energy of the adsorbate species at high temperature ,a decrease in adsorption was absorved [11] .

The study of the temperature effect on adsorption will help also in evaluating the basic therodynamical function (ΔH ,ΔS,ΔG) of the adsorption processes .

These function were estimated through Xm values at different temperatures .

Table (5) gives values at different temperatures for the three surfaces .Plotting (ln X_m) versus (1/T) should produce a straight line with a slope =($-\Delta H/R$) in Figure (9) .

Table (5):Effect of temperature on the maximum adsorbed quantity for adsorption of Fe(III) ion on the three clay.

T.C^o	T.K^o	1000/T $^oK^{-1}$	Attapulgite (C_e=0.12mg/L)		Bentonite (C_e=0.24mg/L)		Kaoline (C_e=0.6mg/L)	
			X_m	lnX_m	X_m	lnX_m	X_m	lnX_m
10	283	3.53	19.9	2.99	6.94	1.94	0.95	-0.05
25	298	3.36	31.2	3.44	6.69	1.90	0.97	-0.03
37.5	310.5	3.22	35.7	3.58	6.32	1.84	0.97	-0.03
50	323	3.10	-	-	6.49	1.87	1.04	0.04

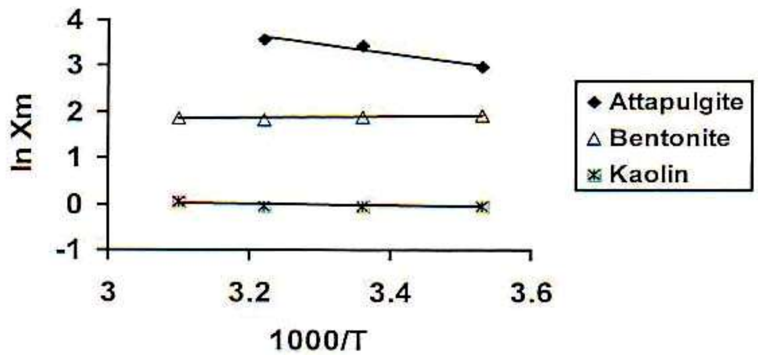


Figure (9):lnX_m plotted against reciprocal absolute temperature for the adsorption of Fe(III) ion on the three surfaces .

Table (6) shows the basic thermodynamic values of adsorption of the ion on (attapulgite ,bentonite and kaolin) ,which calculated by the following relation ships .

The equilibrium constant (K) of the adsorption process at each temperature is calculated from the equation [18] .

$$K = \frac{Q_e * 0.25g}{C_e * 0.0125L} \quad \text{------(1)}$$

Qe :is the amount adsorbed in mg per gram of adsorbent .
Ce : is the equilibrium concentration of the adsorbate expressed in mg/L
(0.25) :represents the weight of the clay that has been used (g) .
(0.0125):represents the volumes of the ion solution used in the adsorption process (L).

The change in free energy (ΔGo) could be determined from the equation [18].

$$\Delta G^o = -RT \ln K \quad \text{------(2)}$$

R:is the gas constant (8.314 J.mol^{-1}.deg^{-1}).
T: the absolute temperature .
The heat of adsorption (ΔH) may be obtained from the equation :

$$\ln Xm = \frac{-\Delta H}{RT} + Cons\tan t \quad \text{------(3)}$$

Xm : is the maximum uptake of adsorption at a certain value of equilibrium concentration (Ce) .

The change in entropy (ΔS) was calculated from Gibbs equation .

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

-------------------------(4)

Table (6) :Values of thermodynamic function of adsorption process of Fe(III) ion on the three clays at 25 C° .

Surface	$\Delta H(KJ.mol^{-1})$	$\Delta G(KJ.mol^{-1})$	$\Delta S(J.mol^{-1}.K^{-1})$
Attapulgite	+0.0160	-21.1981	+71.2081
Bentonite	-0.0016	-15.6583	+52.5436
Kaolin	+0.0015	-8.6096	+28.8993

The negative value of the thermodynamic function (ΔG) for the adsorption of Fe(III) ion on the attapulgite ,bentonite and kaolin indicated that the adsorption process of the ion is spontaneous .

The positive value of entropy for the adsorption of this ion on the three surfaces indicating that the adsorbed species are less ordered on the surfaces .

The positive value (ΔH) for the adsorption of the same ion on attapulgite and kaolin showed that the process is an endothermic ,which suggests that there is a possibility of an ion exchange mechanism taking place [17] .Moreover ,an absorption process may also occur which is usually accompanied by a on bentonite surface was exotherme as shown by the negative value of ΔH .

5- Effect of Ionic Strength

The effect of ionic strength on the removal of Fe(III) ion by adsorption on the three surfaces (attapulgite, bentonite and kaolin) was studied at different concentration of Sodium chloride (0.01-0.03 F) for attapulgite , (0.001-0.0003 F) for bentonite and (0.0001-0.0003 F) for kaoline . The related results are shown in Table (7) .

Table (7) :Adsorption values of Fe(III) ion uptake by three clays at 25 Co from solution of different concentration of sodium chloride .

Attapulgite								
C_o mg/L	Without salt		0.01M Sodium chloride		0.02M Sodium chloride		0.03M Sodium chloride	
	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
400	0.0072	19.9996	0.0216	19.9989	0.0144	19.9993	0.0144	19.9993
600	0.0937	29.9953	0.0216	29.9989	0.0216	29.9989	0.0432	29.9978
700	0.3314	34.9834	0.0216	34.9989	0.0144	34.9993	0.0144	34.9993
750	0.5692	37.4715	0.0288	37.4986	0.0144	37.4993	0.0360	37.4982
800	0.8429	39.9579	0.0288	39.9986	0.0360	39.9982	0.0360	39.9982
Bentonite								
C_o mg/L	Without salt		0.001M Sodium chloride		0.002M Sodium chloride		0.003M Sodium chloride	
	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
100	0.0144	4.9993	0.0576	4.9971	0.0288	4.9986	0.0144	4.9993
110	0.0514	5.4975	0.0576	5.4971	0.0360	5.4982	0.0144	5.4993
120	0.1657	5.9917	0.0648	5.9968	0.0432	5.9978	0.0144	5.9993
130	0.2017	6.4899	0.0648	6.4968	0.0360	6.4982	0.0504	6.4975
140	0.3314	6.9834	0.0793	6.9960	0.0432	6.9978	0.0576	6.9971
150	0.3458	7.4827	0.1657	7.4917	0.1729	7.4914	0.0648	7.4968

C_o mg/L	Without salt C_e mg/L	Without salt Q_e mg/g	0.001M Sodium chloride C_e mg/L	0.001M Sodium chloride Q_e mg/g	0.002M Sodium chloride C_e mg/L	0.002M Sodium chloride Q_e mg/g	0.003M Sodium chloride C_e mg/L	0.003M Sodium chloride Q_e mg/g
160	0.5403	7.9730	1.0735	7.9463	0.2450	7.9878	0.4323	7.9784
170	1.4193	8.4290	1.9092	8.4045	4.5533	8.2723	2.3343	8.3833
Kaolin								
C_o mg/L	Without salt		0.001M Sodium chloride		0.002M Sodium chloride		0.003M Sodium chloride	
	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
5	0.0144	0.2493	0.0288	0.2486	0.0000	0.2500	0.0000	0.2500
10	0.1801	0.4910	0.0360	0.4982	0.0000	0.5000	0.0000	0.5000
15	0.1945	0.7403	0.0432	0.7478	0.0000	0.7500	0.0000	0.7500
20	0.6052	0.9697	0.1513	0.9924	0.0072	0.9996	0.0000	1.0000
25	3.9265	1.0537	0.7565	1.2122	0.3746	1.2313	0.3890	1.2305
30	6.5202	1.1740	1.3905	1.4305	1.1383	1.4431	1.1671	1.4416
35	10.4467	1.2277	5.8285	1.4586	4.7839	1.5108	2.4856	1.6257
40	13.5879	1.3206	8.5807	1.5710	8.1988	1.5901	7.2839	1.6358

***Particle size (75 µm)**

The adsorption of Fe(III) ion on the three clays appeared higher in presence of different concentration of NaCl as compared with the salt free solution .

The effect of increasing the ionic strength on the attapulgite and bentonite surfaces showed no significant effect in the amount of adsorption Fe(III) ion .These results may be due to the presence of low concentration of the ion in solution at equilibrium , where the competition between the ion (Fe^{+3}) and the dissolved ions (Na^{+} , Cl^{-}) for the solvent molecules in the solution is not significant due to the high concentration of free solvent molecules . Moreover ,the strong forces acting between the surface of the clays and the ion may play an important role in this process (19) .So as an absorption process may occur which accompanied the adsorption process .

On the other hand ,the adsorption of Fe(III) ion on the kaolin surface show slight increase in adsorption capacity with increasing the ionic strength ,this effect are two –fold .Based on the Guoy – Chapman theory ,when solid phase and liquid phase are in contact ,they are bound and 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 the diffuse double layer .Such compression help the clay particle and Fe(III) ion to approach each other more closely .These results show that electrostatic attraction plays a significant role in the removal of Fe(III) ion by kaolin (11) .

The second case can be due to the solubility of ionic salt in aqueous media is higher than Fe(III) ion ,therefore ,a competition between them to interact with the solvent molecules lead to an increase in the attraction between the clay surface and the Fe(III) ion (20) .

Plotting the relation ship between the quantity of adsorbate (Q_e) and the ionic strength (I) lead to obtain the following proposal empirical equation **:**

$$Q_e = Q_e{}^{o} - AI \quad \text{---------------------------------(5)}$$

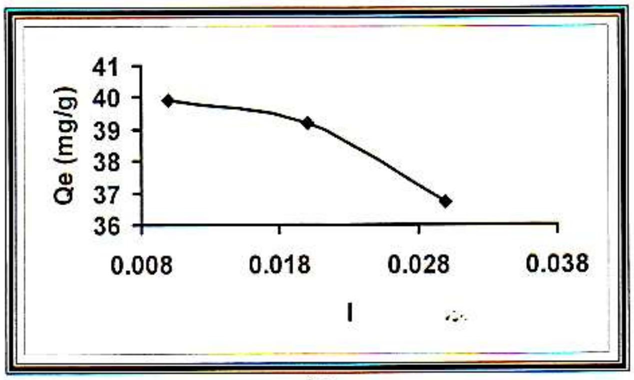
Qe : represent the amount of adsorption at ionic strength =0

A : empirical constant for the system .

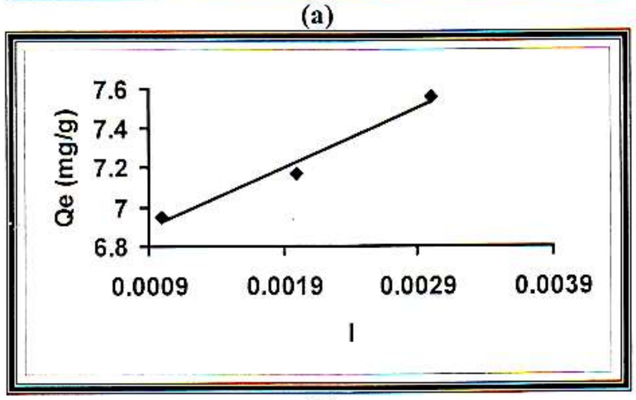
Table (8) and Figure (10) illustrate the relation ship between (Q_e) and (I) on the three clays at 25 C^o.

Table (8) :The effect of ionic strength on the adsorption uptake of Fe(III) ion on the three clays at 25 C^o .

Attapulgite (C_e=0.029 mg/L)		Bentonite (C_e =0.09 mg/L)		Kaolin (C_e =5.8 mg/L)	
I	Q_e	I	Q_e	I	Q_e
0.01	39.9	0.001	6.95	0.0001	1.45
0.02	39.2	0.002	7.17	0.0002	1.54
0.03	39.7	0.003	7.56	0.0003	1.65



(a)



(b)

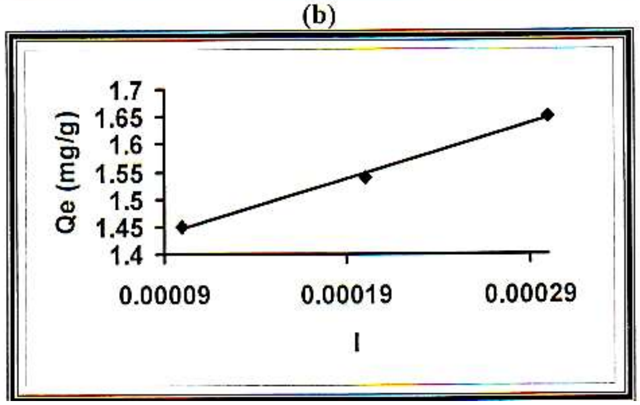


Figure (10) :The relation ship between Q_e and I for (a) attapulgite ,(b) bentonite and (c) kaolin .

As seen in Figure (10) the empirical equation was fully applied on bentonite and kaolin (linear relation ship) and does not applied on attapulgite .The values of Q_e^o and A were found to be 6.62 ,305 for bentonite and 1.35 ,1000 for kaolin respectively .

6- Effect of the Particle Size (Surface Area)

The effect of particle size on the adsorption efficiency of the three surfaces (attapulgite ,bentonite and kaolin) was studied at different particles size (75 ,150 and 250 µm) by using a fixed concentration of Fe(III) ion .

Figure (11) demonstrate the effect of the particle size on the adsorption uptake of Fe(III) ion by the three clays at 25 C^o .

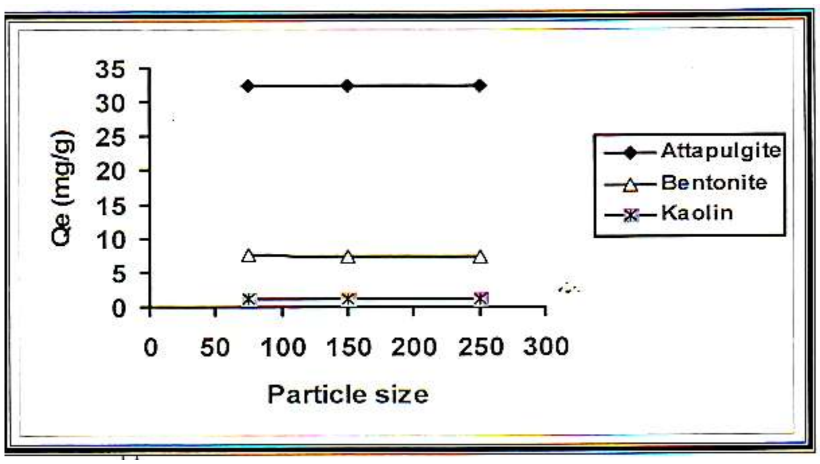


Figure (11) :Effect of the particle size in adsorption uptake of Fe(III) ion on the three clays at 25 C^o .

The results indicated that the increase in the surface area (decrease in the particle size) lead to an increase in the adsorption uptake of Fe(III) ion on the three surface .These results can be attributed to the increase in the active sites exposed to the adsorbate .Subsequently ,the increase in active sites of the surface will lead to an increase in the adsorptive capacity [21] .

7- Effect of the Adsorbent Weight

The effect of the adsorbent weight on the adsorption extent of Fe(III) ion on the three surfaces (attapulgite ,bentonite and kaolin) has been studied at different weight of the clays (0.05 ,0.1 ,0.15 ,0.2 ,0.25 ,0.3 ,0.35 and 0.4 g) by using a fixed concentration of the ion .

Figure (12) show the effect of the adsorbent weight on the quantity of ion adsorbed at 25 C^o **.**

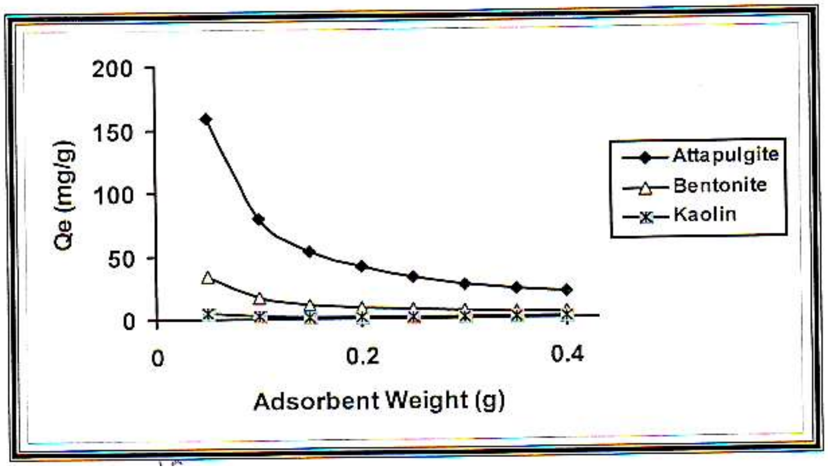


Figure (12) :Effect of the adsorbent weight on the adsorption uptake of Fe(III) ion on the three clays at 25 C^{o} .

As can be seen from the results the curves approach to the plateau region with increasing the adsorbent weight .The plateau value represent the amount of the adsorbent at saturation stage ,which depends on the physically properties of the clay .The plateau values for the three surface (attapulgite ,bentonite and kaolin)were found to be (0.25 ,0.2 and 0.2 g) respectively .

8- Effect of Synergism

The effect of synergism on the adsorption extent of Fe(III) ion on the clays was investigated by mixing equal amounts of two clays and by using a fixed concentration of the ion .

The data related to the effect of synergism are shown in Table (9)

Table (9) : Effect of synergism on the adsorption uptake of Fe(III) ion on the clays at 25 C^{o} .

C_o=700mg/L		(C_o=150mg/L)		(C_o=40mg/L)	
Surface	Q_e mg/g	Surface	Q_e mg/g	Surface	Q_e mg/g
Attapulgite	34.9834	Bentonite	7.4827	Kaolin	1.3206
Attapulgite + Bentonite	34.2799	Bentonite + Attapulgite	7.4996	Kaolin + Attapulgite	1.9993
Attapulgite + Kaolin	34.2799	Bentonite + Kaolin	6.7799	Kaolin + Bentonite	1.9986

***Particle size (75 µm)**

The results showed that mixing of kaolin with attapulgite or with bentonite ,enhanced the adsorption process of Fe(III) ion on the kaolin surface ,also when mixing bentonite with attapulgite at (C_o=150 mg/L) ,enhanced the adsorption process of Fe(III) ion on bentonite surface .

These results may be due to the (Imbibition process) at certain condition .This process lead to swell the clay and it is greatly clear in dilute solution .The continuance swelling reduces the osmotic pressure between clay platelets and the surrounding solution and that weaken the bonds between these platelets or may be broken ,which leads to change the pores geometry of the clay ,causing an increase .

On the other hand ,mixing of attapulgite with bentonite or with kaolin reduces the adsorption amount of Fe(III) ion on attapulgite surface ,that also occur when bentonite is mixed with kaolin at (C_o= 150 mg/L) .

Conclusions :

1- The three clays in this study (Attapulgite ,Bentonite ,and Kaolin) have a high ability for adsorbing the Fe(III) ion from aqueous solution ; however ,attapulgite has the highest ability .

2- The ability of these surfaces for the adsorption of the ion was in the following :
Attapulgite > Bentonite >Kaolin

3- Adsorption isotherm of Fe(III) ion on the three surfaces of Attapulgite and bentonite obeyed Longmuir relation .

4- Results concerning the effect of pH on the adsorption of the on the different surfaces showed an increase in the quantity of the ion adsorbed with increasing pH values on bentonite and kaolin, but reverse effect has absorved on attapulgite

5- Results concerning the effect of temperature on the adsorption process revealed that , the change in temperature has a little effect on the extent of adsorption uptake of De(III) ion on the three clay .Slight decrease in the quantity of ion adsorbed on bentonite ,whereas slight increase in the quantity of ion adsorbed on attapulgite and kaolin .This little effect of temperature on adsorption reflecting a relatively strong forces binding the ion to the clays surfaces which serve the aim of this study in using these clays as material for the pollution .

6- Results concerning the effect of increasing ionic strength of the solution on the adsorption of Fe(III) ion indicated slight increase in the quantity of the ion adsorbed on kaolin and there was in signification change on attapulgite and bentonite.

7- The adsorption amount of Fe(III) ions on the three clays decrease with increasing particles size.

8- At fixed concentration of Fe(III) ion for kaolin that mixed with attapulgite or with bentonite was enhanced the adsorption process of Fe(III) ion on the kaolin surface .The reverse effect has been observed by mixing attapulgite at fixed concentration of Fe(III) ion for bentonite that mixed with attapulgite enhanced the adsorption process of the ion on bentonite surface ,whereas the reverse effect has been noticed by mixing bentonite with kaolin.

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