Adsorption of Fe^{+3} , Cr^{+3} , Cd^{+2} ions from aqueous solution on red Kaolin

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(Recevied on 21/10/2009) **(Accepted for publication 20/4/2010)**

Abstract

In this study the adsorption of Fe^{+3} , Cr^{+3} , Cd^{+2} ions on Red Kaolin from an aqueous solution was studied . The effect of various operation variable mainly adsorbate concentration, adsorbent dosage, temperature , PH and contact time of ions were evaluated . The optimum contact time to attain equilibrium at 90min of Cr^{+3} ion , 60min of Fe^{+3} ion , and 120min of Cd^{+2} ion , and the maximum of adsorbent dosage was 0.1gm of Cr^{+3} , Cd^{+2} and Fe^{+3} and the best PH values in the range (2-14) , the result showed in PH optimum at pH = 6 of Cr^{+3} , pH = 2 of Fe^{+3} and pH =3 of Cd^{+2}. The effect of temperature and thermodynamic parameters wear also studied , the adsorption amount was increased with increased the temperature and the reaction was endothermic . The adsorption isotherms data was analyzed using the Freundlich and Langmuir .

Key word:- Cr^{+3} , Fe^{+3} , Cd^{+2} ion , Adsorption Freundlich and Langmuir isotherm.

الخلاصة

في هذه الدراسة تم امتزاز الايونات Cr^{+3} , Fe^{+3} , Cd^{+2} من المحاليل المائية على سطح الكاؤولين الأحمر ، وتم تأثير العوامل الآتية من الامتزاز هي تركيز المادة الممتزة تركيز المادة ألمازة ، درجة الحرارة ، الدالة الحامضية وزمن الاتزان .فكان أعظم زمن للاتزان عند 90 دقيقة لايون الكروم الثلاثي ، 60 دقيقة لايون الحديد الثلاثي و120دقيقة لايون الكادميوم الثنائي عند أعظم وزن لامتزاز الايونات (0.1 غم)، وتـم دراسة تأثير الدالة الحامضية وبالمدى (2-14) وأشارت النتائج إن أعظم دالة حامضية لايون الكروم الثلاثي هي pH=6 ، لايون الحديد الثلاثي pH=2 ولايون الكادميوم الثنائي pH=3. وتـم دراسـة تـأثير درجـة الحرارة والدوال الثرموديناميكية فوجد إن كمية الامتزاز تزداد بزيادة درجة الحـرارة أي التفاعـل مـاص للحرارة وكما تم تحليل النتائج في ضوء معادلتي فرندلش ولانكماير .

Introduction

The presence of heavy metals with its intrinsically undesirable effects in the environment cannot be overemphasized. The genuine concern of researchers has over the years led to the development of techniques for the removal of these pollutants from wastewater [1] . Notable among these methods are hydroxide precipitation Sulphide or Carbonate precipitation , complexation – ultra filtration , solvent extraction , Chemical metal reduction , granular activated Carbon , reverse osmosis and the novel magnetic separation techniques [2-6]. These methods are relatively expensive involved either elaborate and costly equipment or high problems [7] .

Among may heavy metals, cadmium is one of the well-known toxic heavy metals and is attraction wide attention of environmentalists . Adverse health effect due to Cd^{+2} are well documented and it has been reported to cause renal disturbances, lung insufficiency , bone lesions , cancer and hypertension in Humans [8-9] In general , an adsorbent can be assumened as low cost if it requires little processing , is abundant in nature , or is a byproduct or waste materials from another industry [10], Cr^{+3} toxicity is negligible because it often insoluble hydroxides at circumneutral pH [11] . Cd^{+2} , Fe^{+3} are two of those elements which are essential is small amount for functions , but in high concentrations in case of environmental pollution they are toxic[12]. The variety of materials tested as Cr^{+3} adsorbents includes algae [13,14] , charcoal , wood , pine , olive cake , sawdust , almond shells , cactus leaves[15] , rice husk [16], three aquatic macrophytes [17] adsorption of Cd^{+2} on very surface of Lalang Leaf powder [9], soil min erals [18], EDTA-modified maize cob[19] , Adsorption of Fe^{+3} on activated Carbons [20] , chitosan [21] , acid active Carbon [22].

The clay minerals in soil play the role of a natural scavenger by removing and accumulating contaminants in water passing through the soil [23]

Materials and Methods

Materials

($CrCl_3.6H_2O$,$CdCl_2.H_2O$) from B.D.H. (97% Purity),and($Fe_2(SO_4)_3$) from fluka (98% purity), Kaolin was Baghdad obtained from Iraq[24]. The chemical composition of the Kaolin is given in table (1)

component	Weight %
SiO_2	50.0
Al_2O_3	33.98
TiO_2	33.98
Fe_2O_3	6.17
CaO	0.56
MgO	0.20
K_2O	0.38
Na_2O	0.27
masture	0.08
Lass on ignition	12

Instruments

The following instruments were used through out the work

1. Spectrophotometer T604 ,pg,Instruments ,LTD
2. Blance sensitive –W-Germany
3. PH-meter HANNA,Portugal
4. Oven memmert ,Edelstahi,Germany
5. Shaker Bath ,Indicator GCA,Chicago
6. Centrifugal ,Herouse,septch

preparation of clay powder

Kaolin clay was supplied in the powder from . It was suspended in HCl solution pH=3 to remove carbonate and it was washed with an excess amount of distilled water to remove the soluble materials (25) . The particle size was (600mm)

Preparation of ions solution

Standard stock solution of 500ppmof ions was prepared by dissolving 0.25gm of ions compounds in a minimum amount of distilled water in a 500ml volumetric flask and volume was made up to the mark with distilled water . Solutions of different concentrations were prepared by serial dilutions for ion between (5-50ppm). Absorbance values of these solutions were measured at the selected λ_{max} value for each ion and potted against the concentration values.

The Calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Adsorption studies

All Red Kaolin were used to study adsorption of ions . Adsorption isotherms study of ions was carried out in a 50ml stopper conical flask by adding 0.1gm of Red Kaolin to 35ml of ions solution . The concentration of ions in the ions solution were varied in the range of 5-50ppm . All experiment were done at room temperature often gentle shaking for 90min of Cr^{+3} , 60min of Fe^{+3} and 120min of Cd^{+2} in a shaker both , the contents were filtered through filter paper (Qualitative filter paper). Concentration of ions in the filtrate were then determined by U.V. – Visible spectrophotometer . The amount of ions adsorbed was calculated based on the difference between the ions concentration in aqueous solution before and after adsorption from relation (26) .

$$Q_e = \frac{(C_o - C_e)V(ml)}{M(gm)}$$

Where:-

C_o. and C_e are ions concentration in (mg/L) before and after adsorption for optimum time t, V is the volume of adsorbate in 500ml and m(g) is the weight of the adsorbent .

For adsorption at higher temperature ions solution and Red Kaolin in the conical flasks were shaken in shaker bath maintained at (292 , 302 , 312 , 322 and 332 K) for optimum time of ions . Study of pH solution of ion in the range (2-14) .

Results and Discussion

Adsorption capacity

The results of the experimental runs for the adsorption of Cd^{+2} , Fe^{+3} , Cr^{+3} ions . Red Kaolin of particle size 600µm . These results are presented as fraction of amount adsorbed (Q_e) against equilibrium concentration (C_e) . The amount of ions adsorbed at optimum time and 0.1gm of ions figure (1) . The results indicated also that the adsorption capacity of the adsorbent for the compounds used increase in the following $Cd^{+2}>Fe^{+3}>Cr^{+3}$ this behavior was attributed to various factors the adsorption .

Contact time effect

Figure (2) shows the effect of contact time on removal of ions by

Red Kaolin . The removal efficiency increase with time and attains equilibrium within 60min of Fe^{+3} ion , 90min of Cr^{+3} ion and 120min of Cd^{+2} ion , the removal of ions with time curves are monotonously increase to saturation , since then , the removal efficiency has no change with contact time .

Dosage effect

The effect of varying the dosage of the adsorbent an the removal efficiency of tons from aqueous solution are show in figure(3). The initial PH was adjusted at optimum pH , that Q_e values increase with the increasing of the optimum dosage over the one temperature of solution at 292K. The can be explained by the fact that more mass available , more the contact surface offered to the adsorption . These results are qualitatively in a good agreement with these found in the literature [27].

Adsorption isotherms

The equilibrium removal of the ions considered can be mathematically expressed in terms of adsorption isotherms. Adsorption data are commonly fitted to the freundlich equation as

$$Qe = K_f . C_{eq}^{1/n}$$

Where:- C_{eq} is the equilibrium concentration (mg/L) , Q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption Capacity and intensity respectively . The Linearised from of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as [28] .

$$\text{Log } Q_e = \log K_f + \frac{1}{n} \log C_{eq}$$

The Linear regression equation for the Freundlich adsorption isotherm is shown on figure(4).

The values of K_f and n were calculated from the intercepts and slopes of the Freundlich plots respectively[29] . n values between 1 to 10 beneficial adsorption , states that the values of K_f and n determine the steepness and curvature of the isotherm.

The Freundlich equation frequently gives n adequate description of adsorption data over a restricted rang of concentration, even though it is not based on any theoretical background. Apart from homogenous surface , the Freundlich equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau , indicating a multi-lager adsorption [30].

The Langmiur isotherm represents the equilibrium of ions between the solid and liquid phases . The following equation can be used to equation the adsorption isotherm .

$$Q_e = \frac{K_l \ C_e}{l+a \ C_e}$$

where :- Qe (mg/g) is the amount adsorption

Ce (mg/L) is the ion residual concentration in solution at equilibrium. a and K_l is the constant equation .

The Langmiur isotherm is based on these assumptions[31], ions are chemically adsorbed at a fixed number of well defined sites. , each site can hold only one ion. , all sites are energetically equivalent and these is no interaction between the ions . When the initial ions concentration rises , adsorption increase which the binding sites are not saturated . The linearized Langmiur isotherm allows the calculation of adsorption capacities and the Langmiur constants and its equated by the following equation .

$$\frac{C_e}{Q_e} = \frac{1}{K_l} + \frac{a}{K_l} . Ce$$

From the Linear pbts of C_e/Q_e vs C_e , we calculated the liner regression equations for the Langmiur isotherm for the sorption process K_l and A were obtained from the slope and intercept of the plots figure(5). Table (1) shows constants equation and R^2 of adsorption ion on red Kaolin .

pH effect

The experiments carried out at different pH shows that there was a change in the adsorption amount of ions over the entire pH range of 2 to 14 shown in the figure(6). This indicates the strong force of interaction between the ions and the Red Koalin that , either H^+ or OH^- ions could influence the adsorption capacity. Here the interaction is more at pH = 6 of Cr^{+3} , pH = 2 of Fe^{+3} and pH = 3 of Cd^{+3} , due to the to the competence of acidic H^+ ion with ions cation for the sorption sites . The amount of sorption increased at the above pH values is due to the presence of ionic H^+ groups . The adsorption of ions on the Red Koalin does involve interactions (32) .

Temperature effect

Fig(7) shows the equilibrium removal of ions as a function of the temperature .The initial concentration was fixed 50ppm and optimum PH .Over the dosage of the 0.1gm .it can be seen that the Qe increase as the temperature increase. For example ,at dosage of 0.1gm of red kaolin ,it is found that Qe increase from 5.985mg/g to 11.62mg/g of Cr^{+3} ion, from 10.115mg/g to 12.145mg/g of Fe^{+3} ion and from 13.580mg/g to 15.050mg/g of Cd^{+2} ion ,as the solution temperature increase from 292k to 332k respectively.

This behavior confirms that the adsorption process is endothermic process. The increasing in adsorption as temperature increases may be due to the relative increase in the escaping tendency of ion from the solid phase to solution phase, or due to the weakness of adsorption forces between the active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of adsorbed phase (33)

Thermodynamics parameters

It is important to study the thermodynamics parameters such as Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS change . table(2)

The change in free energy (ΔG) could be determined form the equation

$$\Delta G = -RT \ln \frac{Ce}{Qe}$$

The heat in enthalpy (ΔH) may be obtained from the Vant Hoff 's equation fig(8)

$$\text{Log } X_m = \frac{-\Delta H}{2.303RT} + \text{Constant}$$

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

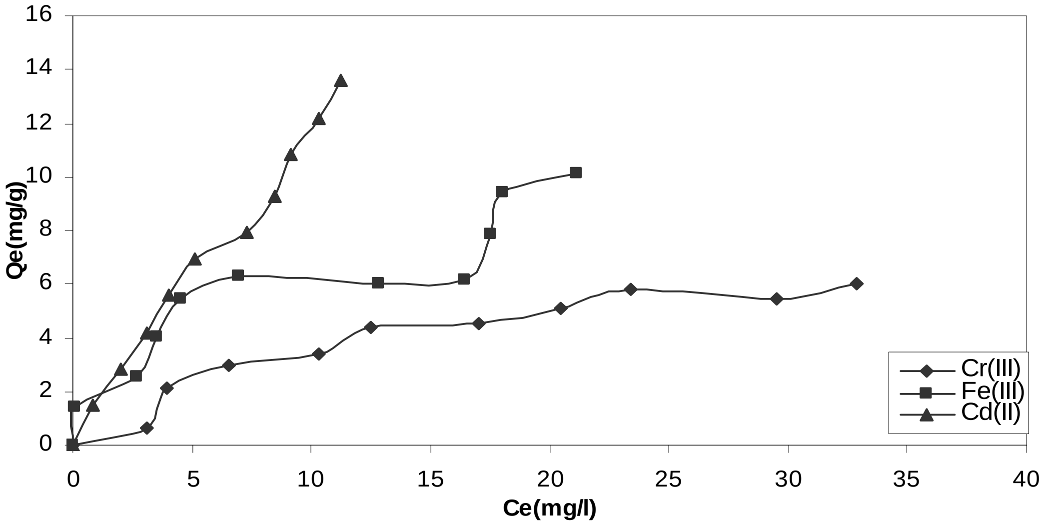
$$\Delta G = \Delta H - T\Delta S$$

Table (1):- Freundlich and Langmuir isotherms for ions using red kaolin at 292K

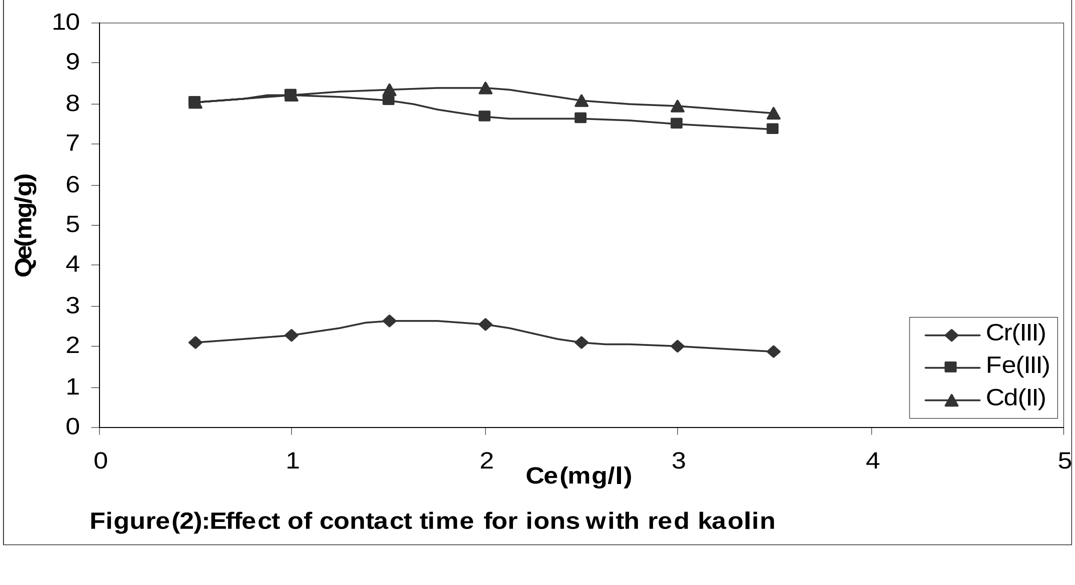
Ions	K_f	n	R^2	a	k	R^2
Cr^{+3}	1.175	2.0911	0.962	0.089	0.704	0.9725
Fe^{+3}	2.045	2.044	0.8215	0.120	1.453	0.8396
Cd^{+2}	1.576	1.153	0.9851	0.047	1.686	0.6915

Table(2):- thermodynamic values and constant of vant Hoff"s equation for ions using red kaolin at 292K

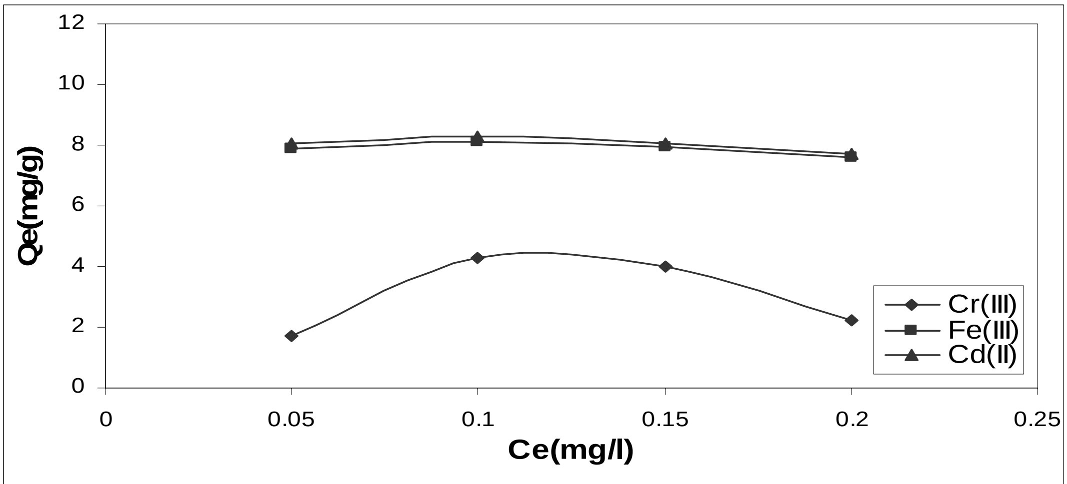
Ions	**ΔH(Kj.mol^{-1}.k^{-1})**	**ΔG(Kj.mol^{-1}.k^{-1})**	**ΔS(j.mol^{-1}.k^{-1})**	**Conc.**
Cr^{+3}	5.877	4.137	5.958	3.222
Fe^{+3}	2.194	1.784	1.404	1.891
Cd^{+2}	9.394	2.943	22.09	1.5138



Figure(1):Isotherms adsorption for ions with red kaolinderived



Figure(2):Effect of contact time for ions with red kaolin



Figure(3):Effect of weight adsorbent for ions on red kaolin

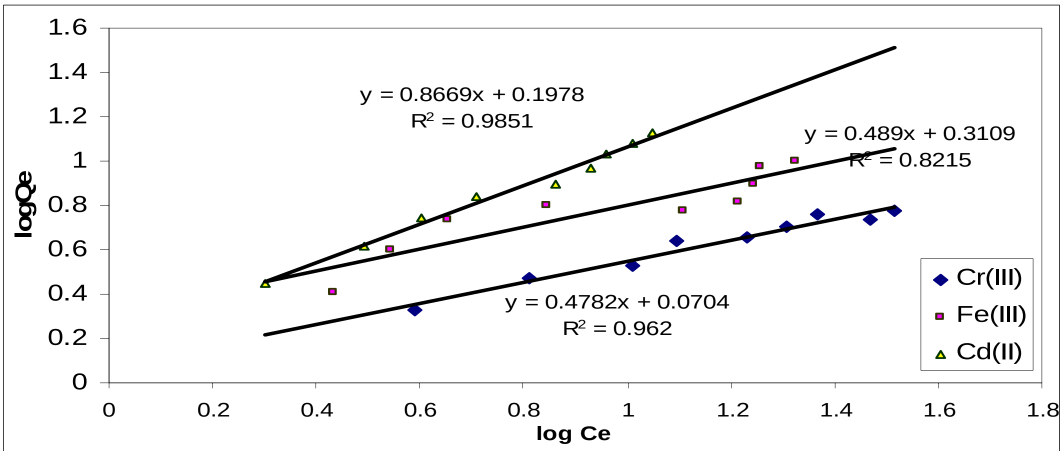


Figure (4):Freundlich adsorption isotherms ions on red kaolin

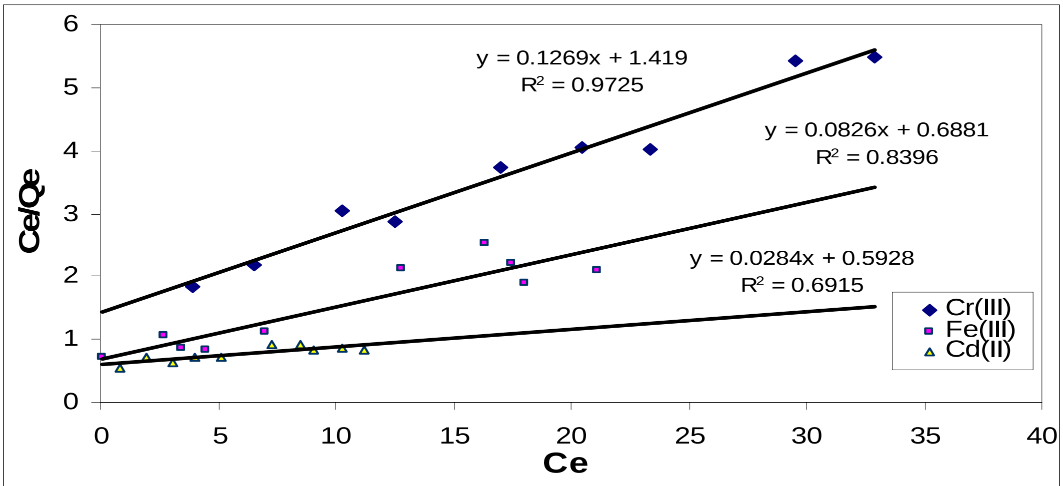
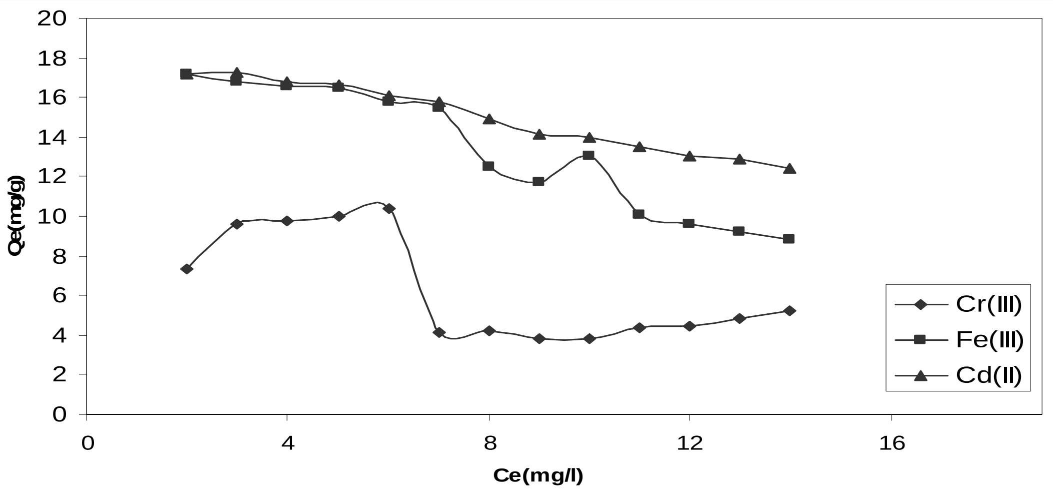
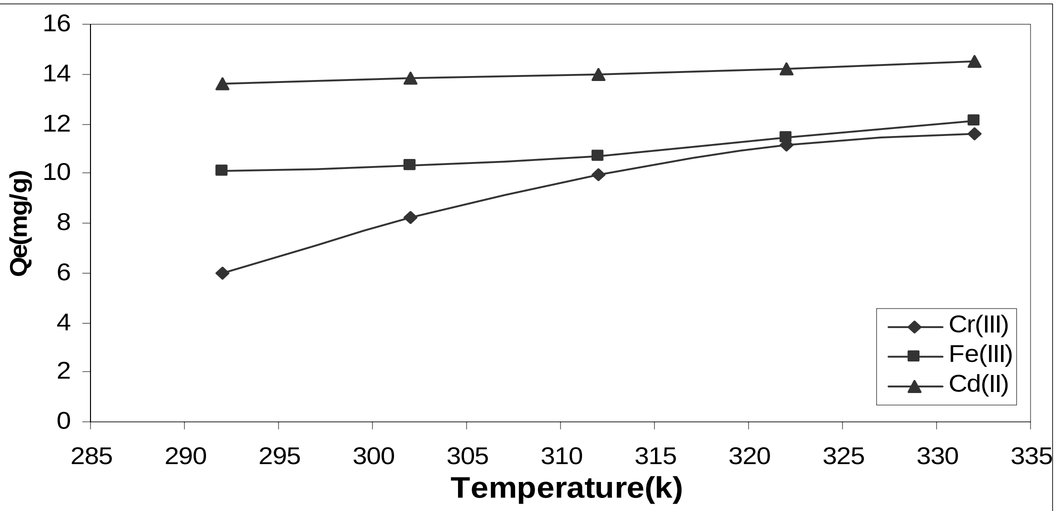


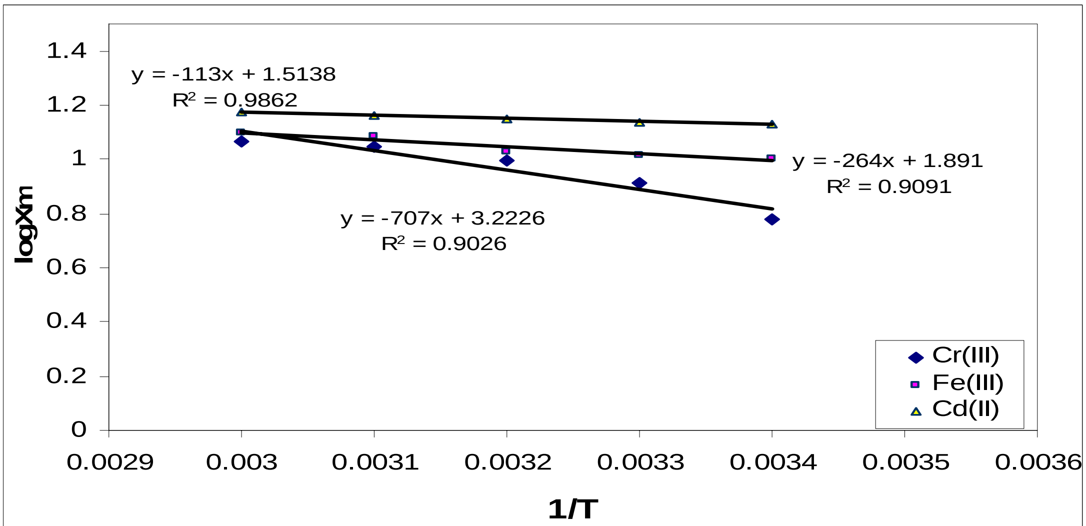
Figure (5):Langmuir adsorption isotherms ions on red kaolin



Figure(6):Effect of PH solution for ions on red kaolin



Figure(7): Effect of temperature of ions on red kaolin



Figure(8):relation between log Xm and 1/T on red kaolin

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