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Kinetic Study for Adsorption of Chromium tri-Oxide CrO_3 on Kaolinite Surface

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Abstract

The removal of CrO_3 by using kaolinite have been investigated, as a function of initial concentration, pH and temperatures.

Adsorption process, was attained to equilibrium within 60 minutes which indicated by uv-visible absorption spectroscopy technique at wave length 390 nm.

The best results which are used in this study were achieved at pH of 4, and 290 K, in this range of pH and temperature, the chromium tri oxide transformation hydro-chromate into bi-chromate takes place.

The equilibrium data for adsorption are fitted to the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm equations. Values of parameters for theses isotherms equations were calculated.

The mean energy of adsorption E_{ads}, was also calculated from the adsorption energy constant K_{eng}, its value determined from the D-R isotherm equation. The temperature thermodynamic parameters like ΔG , ΔH and ΔS have been calculated. Values of enthalpy ΔH showed that the adsorption process is exothermic.

الخلاصة

تمت دراسة ازالة صبغة ثلاثي اوكسيد الكروم بوساطة طين الكاؤلينايت, كدالة للتركيز و الدالة الحامضية ودرجة الحرارة.

وجد ان زمن الاتزان لعملية الامتزاز هو 60 دقيقة والتي حددت باستخدام تقنية مطيافية امتصاص الاشعة المرئية- الفوق البنفسجية عند الطول الموجي 390 نانوميتر.

وجد ان افضل النتائج لعملية الامتزاز هي عند اقل دالة حامضية (pH = 4) ودرجة حرارة المختبر (T= 290 K), وذلك لانه في هذه الدالة سوف يتحول مركب CrO_3 الى CrO_4^{2-} والذي بدوره يتحول الى الهايدروكرومات $HCrO_4^{1-}$ والذي يتحول الى ايون ثنائي الكرومات السالب $Cr_2O_7^{2-}$.

طبق على نتائج الاتزان لعملية الامتزاز معادلات ايزوثرمات الامتزاز وهي (معادلة فرندلج , لانكماير ومعادلة D-R), وقيم ثوابت لهذه المعادلات الايسوثرمية تم احتسابها, والتي من ضمنها معدل طاقة الامتزاز التي تم احتسابها من معادلة D-R .

تم حساب الدوال الثرموديناميكية (ΔS , ΔH , ΔG) بوساطة تاثير درجة الحرارة على عملية الامتزاز ووجد من خلالها ان عملية الامتزاز هي باعثة للحرارة وذلك من خلال قيمة التغير في طاقة الانثالبي القياسية ΔH^0.

Introduction

The adsorption of dyes onto clays has had in the past the unique application of being a rather simple way to determine important properties of clays (1).

Some specific effluents from industrial production processes may be difficult to purify by commercial wastewater treatment technology, as a result of the complexity of some of their components. Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein (2).

The disposal of coloured wastes such as dyes into receiving waters causes damage to the environment as they are toxic to aquatic life. As it is difficult to remove the dyes from effluents, the adsorbent activated carbon is the most widely used for the removal of color from textile effluents, because it has a high capacity for organic matter, but its use is limited due to its high cost (3, 4).

Widespread contamination of soil and groundwater by synthetic organic chemicals (e.g., dyes) has been recognized as an issue of growing importance in recent years. Most of these compounds are potential or known human carcinogens and are of considerable health concern, even at low concentrations. For this reason, the fate and transportation of these compounds has been the subject of much research.

Methods of decolorization have therefore become important in recent years. In principle, decoloration is possible with one or more of the following methods: adsorption, precipitation, chemical degradation, photodegradation and biodegradation (5, 6).

Clays are composed mainly of silica, alumina, and water; frequently with appreciable quantities of iron, alkalis, and alkali earth (7).

The most important clay mineral is kaolinite [$Al_2O_3.2SiO_2.2H_2O$]which is the main composed of kaolinite clay(8). A fine white or greyish white unctuous powder, odourless and almost tasteless. Practically, insoluble in water, organic solvents, mineral acids and solutions of alkali hydroxides(9).

It is important in some industries(10) and in some preparations, chromium (VI) compounds are strong oxidizing agents and are highly corrosive. In the environment, they generally are reduced to chromium (III) compounds. The chromium (VI) compounds most commonly encountered in industry are calcium chromate, chromium trioxide, sodium chromate and dichromate, potassium chromate and dichromate, lead chromate, strontium chromate, and zinc chromate.

Chromium(VI) compounds are widely used as corrosion inhibitors, the manufacture of pigments, metal finishing and chrome plating, stainless-steel production, leather tanning, and as wood preservatives, Chromium(VI) compounds also are used in textile dyeing processes, printing inks, drilling mud, pyrotechnics, water treatment, and chemical synthesis.(11)

Materials and methods

Materials

Chromium tri-oxide obtained from B. D. H., (99% purity), kaolinite was obtained from the general company for Geological Survey and Mining, Baghdad, Iraq, have the general structure consisting mainly [$Al_2O_3.2SiO_2.2H_2O$](12) the chemical analysis of kaolinite is listed in table (1).

Table 1. The Chemical analysis of kaolinite

Constituent	Wt% .
SiO_2	54.68
Al_2O_3	30.19
Fe_2O_3	1.02
TiO_2	1.00
Loss on ignition	10.94
Total	97.83

Kaolinite sample has been treated before using as follows (13): it was suspended in HCl solution of pH of 3 to remove carbonate of, it was washed with an excess amount of distilled water to remove soluble materials. Then it was dried in the oven at 383K for ten hours, ground then sieved by 90 µm sieve, 200 mesh. The Particles under 90 µm are used in further experiment.

Spectronic – 21 mode u.v-visible single beam with 1 cm cells Bausch and lomb (USA) was used for all absorbance measurements, pH measurements were made with Knick digital pH meter (England) model, and shaker water bath, SB. 4, Tecam were used.

Methods

The adsorption isotherms have been determined by mixing the chromium tri-oxide (VI) solution of known initial concentration with accurately weighed amount of kaolinite in a tightly closed flask at certain temperature and pH.

The amount of kaolinite in the slurry was 0.25 gm / 250ml solution. A constant mixing at a constant temperature and pH was achieved using a shaker water bath. The kaolinite – solution have been then equilibrated for 2 hours, clay suspensions have been then filtered and the supernatant solution was subjected to analysis using ultraviolet – visible absorption spectroscopy technique (uv - visible) at 390 nm. the amount of chromium tri-oxide (VI) retained by Kaolinite was calculated from the relation :

$$Qe = \frac{(C_o - C_e)V}{m} \quad ....(1)$$

Where C_o is the initial concentration and C_e is the equilibrium concentration (mg/L) and V(L) is the total volume of chromium tri-oxide (VI) and m (gm) is the weight of kaolinite, the same experiment was repeated at different conditions of initial concentrations, temperature and pH medium.

Results and Discussion

Adsorption isotherms:

The obtained experimental equilibrium data for the adsorption of chromium tri-oxide (VI) by kaolinite clay at the different temperature 290K, 300K and 310 K are presented in figure (1). The adsorption isotherms were measured at a constant initial pH of 4.

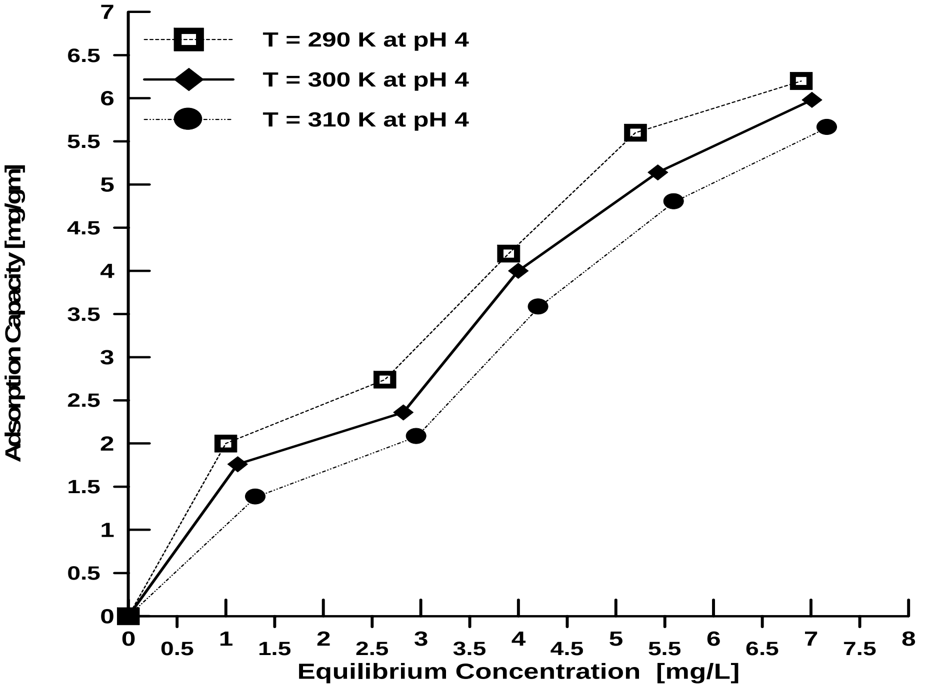

Figure 1: adsorption isotherms of chromium tri-oxide (VI) by kaolinite at pH 4.

The considerable increases in the amount of chromium tri-oxide (VI) adsorbed with decreases in temperature, is attributed to the possible decrease in the number of active sites available for adsorption on the surface, also increasing of temperature caused increase the kinetic energy of adsorbate molecules and hence the increasing of probability of desorption of molecules from surface and migrate to bulk confirms the exothermic nature of the process(14, 15).

Effect of pH:

The adsorption isotherms at various pH media (4, 7 and 10) are shown in figure (2). It is seen that the adsorbed amount of chromium tri- oxide (VI) on kaolinite has decreased with increasing pH values, because at lower pH chromium tri-oxide (VI) appears as single- valued anion $HCrO_4^{-1}$ (16)

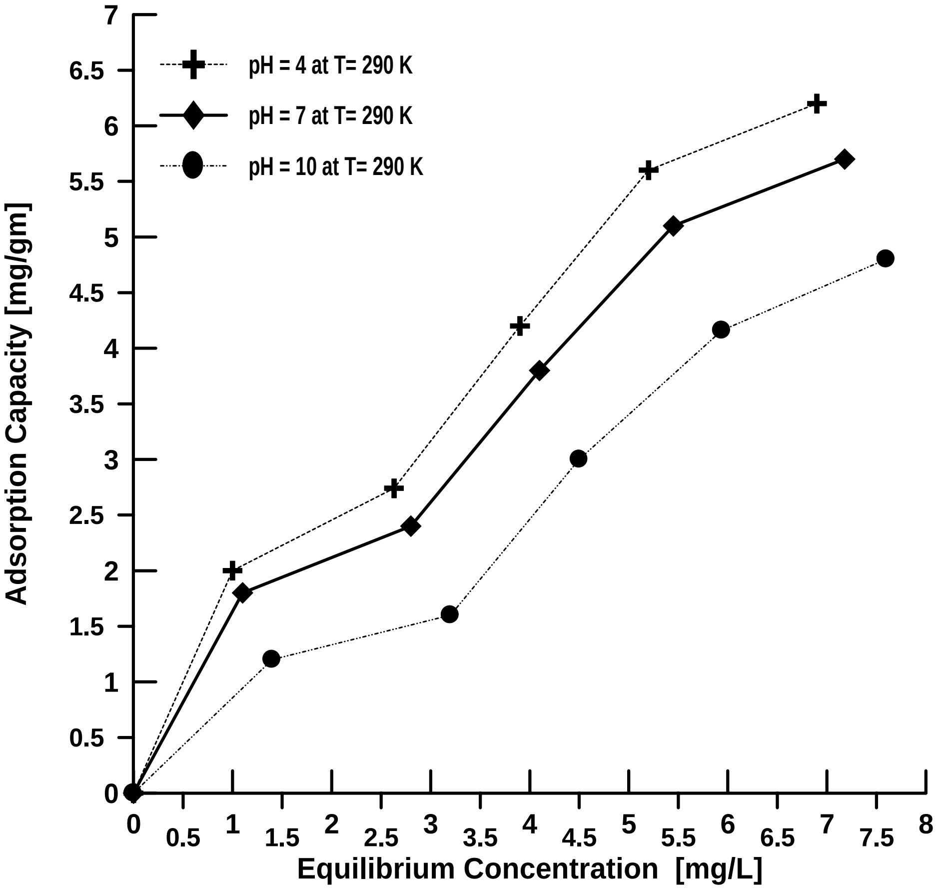

Figure 2: adsorption isotherms of chromium tri-oxide (VI) by kaolinite at different temperatures.

Thermodynamic parameters:

The thermodynamic parameters for the adsorption of chromium tri-oxide (VI) by kaolinite such as the standard enthalpy change (ΔH), the standard Gibbs energy change (ΔG) and the standard entropy change (ΔS) can be calculated from the variation of maximum adsorption with temperature (T) using the following basic thermodynamic relations (17):

$$\ln K_e = A - \frac{\Delta H}{RT} \text{...........}(2)$$

$$\ln K_e = -\frac{\Delta G}{RT} \text{...............}(3)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T} \right) \text{.......}(4)$$

According to equation 2, the mean of the enthalpy change due do the adsorption of chromium tri-oxide (VI) by kaolinite over the temperature range studied can be determined graphically figure (3) by the linear plotting of lnX_m against 1/T using the least squares analysis.

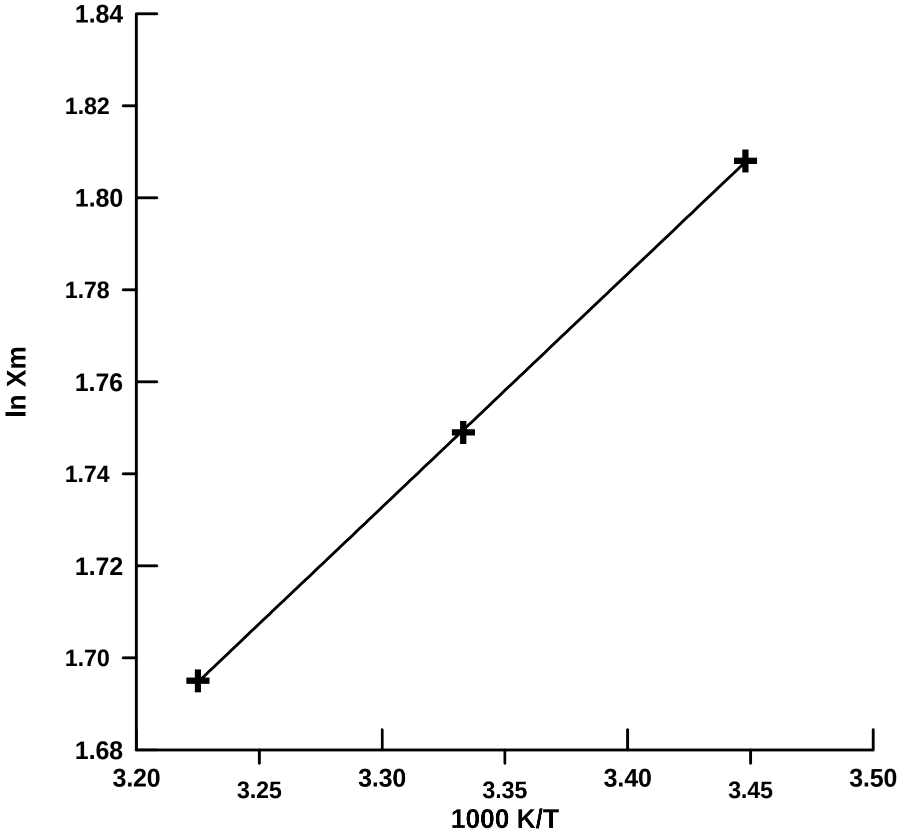

Figure 3: Van't Hoff equation for adsorption of chromium tri-oxide (VI) on kaolinite surface .

An important result can be obtained from table 2 is that the Gibbs energy (ΔG) is small and negative with its value decreases with increasing temperature.

This indicates that the adsorption processes of chromium tri-oxide (VI) by kaolinite can be enhanced by decreasing temperature.

The values of entropy change (ΔS) are positive, the negative values of enthalpy change (ΔH) show the exothermic nature of the adsorption process of chromium tri-oxide (VI) by kaolinite.

Table 2: The thermodynamic parameters for the adsorption of chromium tri-oxide (VI) on the Kaolinite.

pH 4 T/K	Thermodynamic parameters		
	ΔH (kJmole^{-1}) Mean value	ΔG (kJ mole^{-1})	ΔS (JK^{-1} mole^{-1})
290	-0.5017	-1.413	3.142
300		-1.332	2.767
310		-1.177	2.178

Isothermal analysis:

Freundlich, Langmuir and Dubinin-Radushkevich (D-R) adsorption isotherm models were applied to the system, studied at three temperatures (290K , 300K and 310K) and at different pHs (4, 7 and 10).

Freundlich isotherm: adsorption data fitted to the linear form of the Freundlich isotherms is expressed as(17, 18):

$$Q_e = K_f * C_e^{1/n} \quad ....(5)$$

Where Q_e is the equilibrium adsorption capacity (mg/gm), Freundlich constant K_f and the adsorption intensity, 1/n are directly obtained from the slopes and the intercepts of the linear plot, respectively in table (3), the K_f, which is a measure of adsorption capacity, decreased with temperature and pHs increased. Freundlich equation in logarithmic form can be written as follows:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e ....(6)$$

(ln Q_e versus ln C_e), are shown in figure (4 and 5) is linear indicating the applicability of Freundlich adsorption isotherm (19-21) $0.9071 \langle R^2 \langle 0.9387$,for different temperature and $0.9146 \langle R^2 \langle 0.9387$,for different pH media.

The magnitude of the power, n gives an indication of the favorability and capacity of the adsorbent/adsorbate system(17), Treybal has reported that "n" values between 1 and 10 represented favorable adsorption conditions(22). In all cases reported here, the power is $1 \langle n \langle 2$ showing beneficial adsorption for the system and the fit of the data to the Freundlich model indicate that the forces of adsorption by kaolinite are governed by physic-sorption(23, 24).

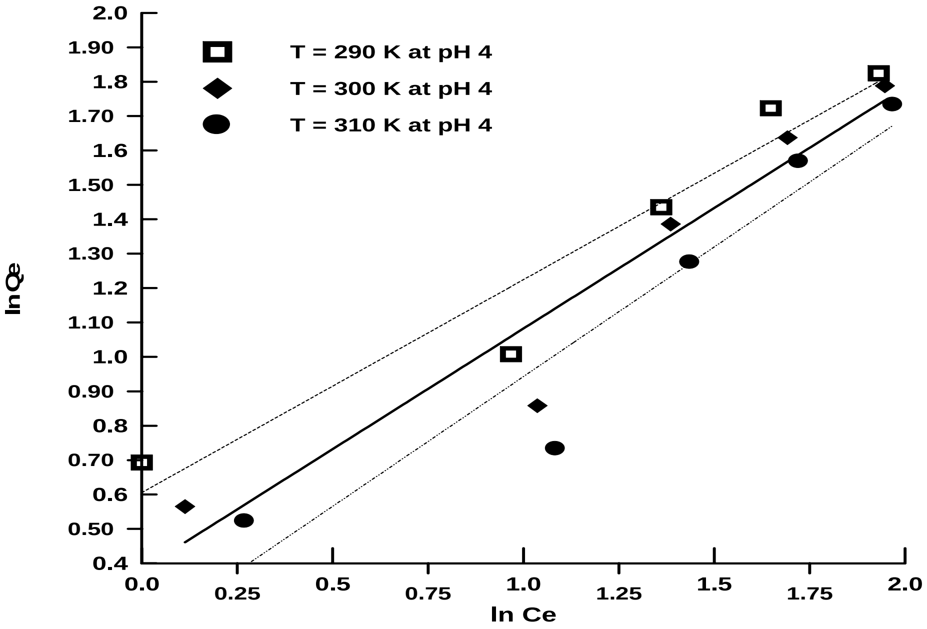

Figure 4: Freundlich plots Kaolinite / chromium tri-oxide (VI) at different temperature and pH 4.

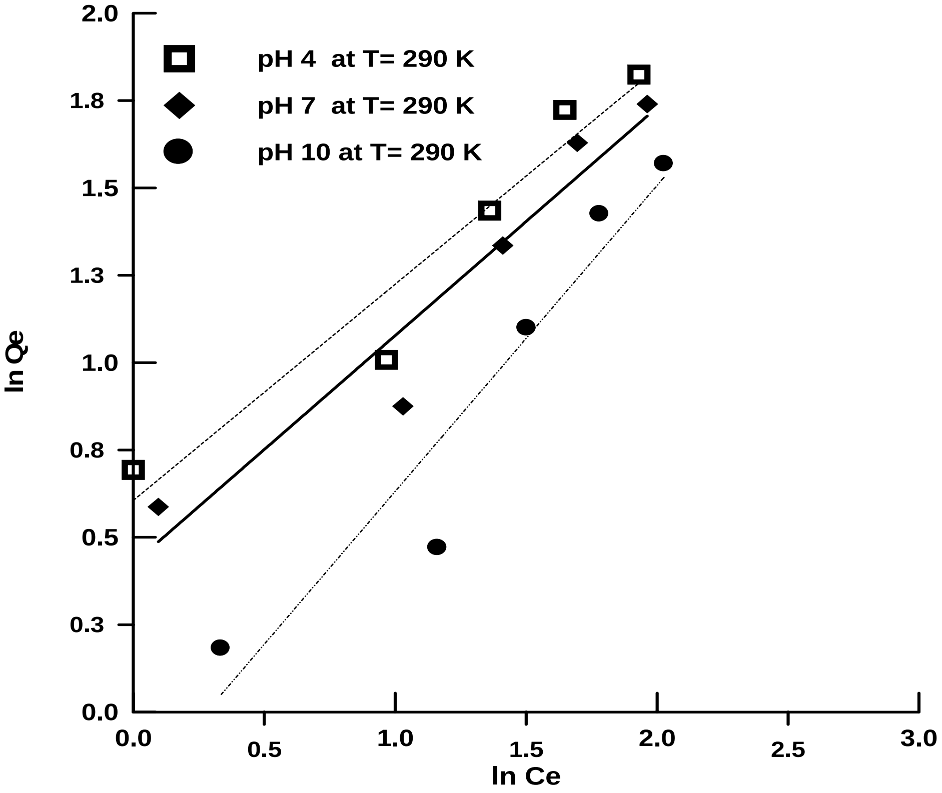

Figure 5: Freundlich plots Kaolinite / chromium tri oxide (VI) at different pHs.

Langmuir isotherm: chromium tri-oxide/kaolinite system not obey very well the Langmuir adsorption isotherm, the Langmuir equation is the mathematical function most commonly used to describe this process(25).

The Langmuir isotherm can be expressed as:

$$Q_e = \frac{X_m k C_e}{1 + kC_e} \text{.............}(7)$$

where Q_e = equilibrium amount of chromium tri-oxide (VI) adsorbed per unit weight of adsorbent (mgg^{-1}), C_e =concentration of chromium tri-oxide (VI) remaining in solution at equilibrium (mgL^{-1}), Xm =amount of chromium tri-oxide (VI) adsorbed per unit weight of adsorbent for forming a complete monolayer on the surface (mgg^{-1}) and k is a constant related to the energy. By plotting Q_e versus C_e, a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering(26).

The linear form of the Langmuir isotherm equation is represented in equation (8).

$$\frac{C_e}{Q_e} = \frac{1}{kX_m} + \frac{C_e}{X_m} \text{.............}(8)$$

Straight lines were obtained by plotting C_e / Q_e against C_e for the adsorption of chromium tri-oxide (VI) on kaolinite illustrated in figures (6 and 7) at different temperatures and pH media.

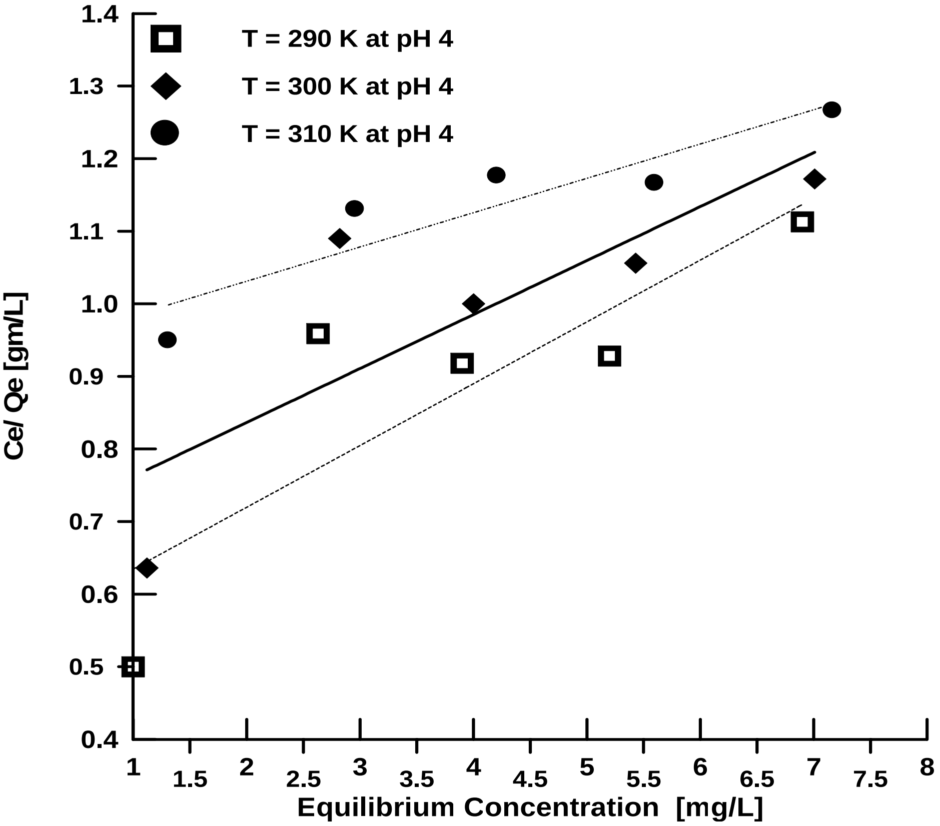

Figure 6: Langmuir plots Kaolinite / chromium tri-oxide (VI) at different temperature and pH 4.

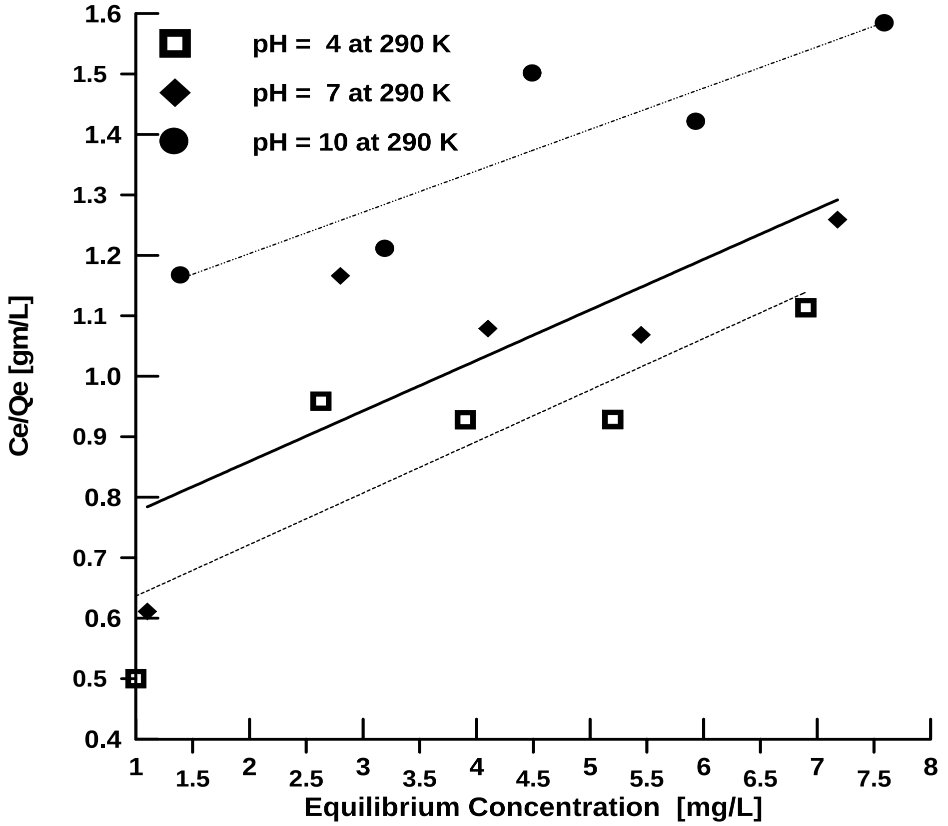

Figure 7: Langmuir plots Kaolinite / chromium tri-oxide (VI) at different pHs.

The values of X_m and k calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients R^2; are reported in Table 3.

As it can be seen most of the adsorption isotherms obeyed the Langmuir equation with correlation coefficients $R^2 > 0.6132$. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage(18).

The equilibrium adsorption density *Qe* increased with the increase in chromium tri-oxide (VI) concentration.

the equilibrium adsorption densities *Qe* on the kaolinite reach almost the same *Qe* as those at high equilibrium chromium tri-oxide (VI) concentrations.

It indicates that the kaolinite have high adsorption density even at low equilibrium chromium tri-oxide (VI) concentrations(27).

Table 3: Langmuir and Freundlich constants for adsorption of chromium tri-oxide (VI) at different temperatures and pHs.

pH 4 **T/K**	**Langmuir constants**			**Freundlich constants**		
	Xm (mg/gm)	**K_L (L/gm)**	**R^2**	**K_f (L/gm)**	**1/n**	**R^2**
290	11.74	0.154	0.717	1.832	0.618	0.9387
300	13.45	0.108	0.664	1.464	0.701	0.9249
310	21.16	0.05	0.847	1.207	0.754	0.9071
290K **pH**	**Langmuir constants**			**Freundlich constants**		
	Xm (mg/gm)	**K_L (L/mg)**	**R^2**	**K_f (L/gm)**	**1/n**	**R^2**
4	11.74	0.154	0.717	1.832	0.618	0.9387
7	11.98	0.121	0.613	1.528	0.652	0.9277
10	14.62	0.064	0.815	0.783	0.875	0.9146

Dubinin Radushkevich (D-R):

The adsorption data were also tested for another adsorption isotherm, the Dubinin Radushkevich (D-R) (20).

This isotherm is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential. The D-R equation is

$$Q = \bar{X}_m \exp(-\bar{K}\varepsilon^2)............(9)$$

where ε (polanyi potential) = RT ln (1+1/C_e), Q_e is the equilibrium amount of chromium tri-oxide (VI) adsorbed per unit weight of kaolinite (mg gm^{-1}), Xm is the adsorption capacity (mg gm^{-1}), C_e is the equilibrium concentration of chromium tri-oxide (VI) in solution (mg L^{-1}), $\bar{K}$ is the constant related to the adsorption energy (mol^2 kJ^{-2}), R is the gas constant (0.008314 kJ K^{-1} mol^{-1}) and T is the temperature (K). The D-R isotherm can be linearized as

$$\ln Q_e = \ln \bar{X}_m - \bar{K}\,\varepsilon^2 ....(10)$$

The plots of lnQ_e *against* ε^2 are shown in Figures (8 and 9) at different conditions from temperature and pH.

Most of the adsorption isotherms fitted the D-R equation with correlation coefficients $R^2 \rangle 0.989$, by making certain assumptions, the mean energy of adsorption, E_{ads}, can be calculated from the K values (19)

using the relation $E = (2K)^{-0.5}$, values of E are presented in table 4 The calculated mean energy of adsorption, E, from the D-R isotherm, gives information about the chemical or physical properties of the sorption.

The calculated mean energy values of adsorption of chromium tri-oxide (VI) by kaolinite are very small and this implies that the type of adsorption is physical.

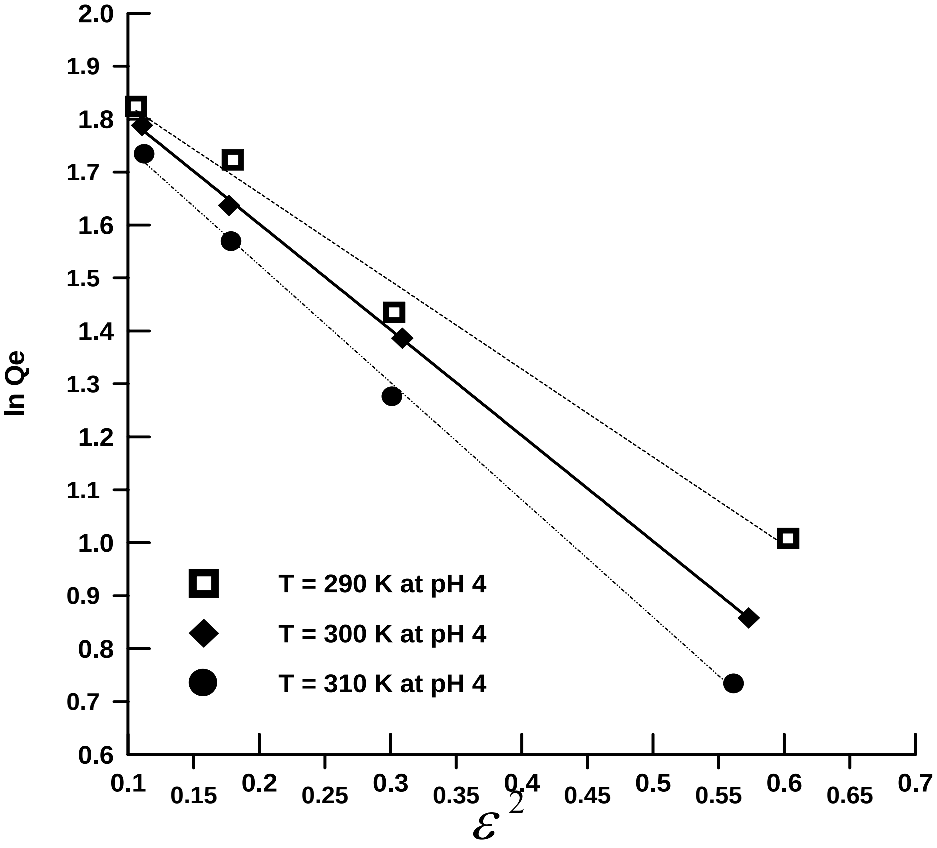

Figure 8: D-R plots Kaolinite / chromium tri-oxide (VI) at different temperatures and pH 4.

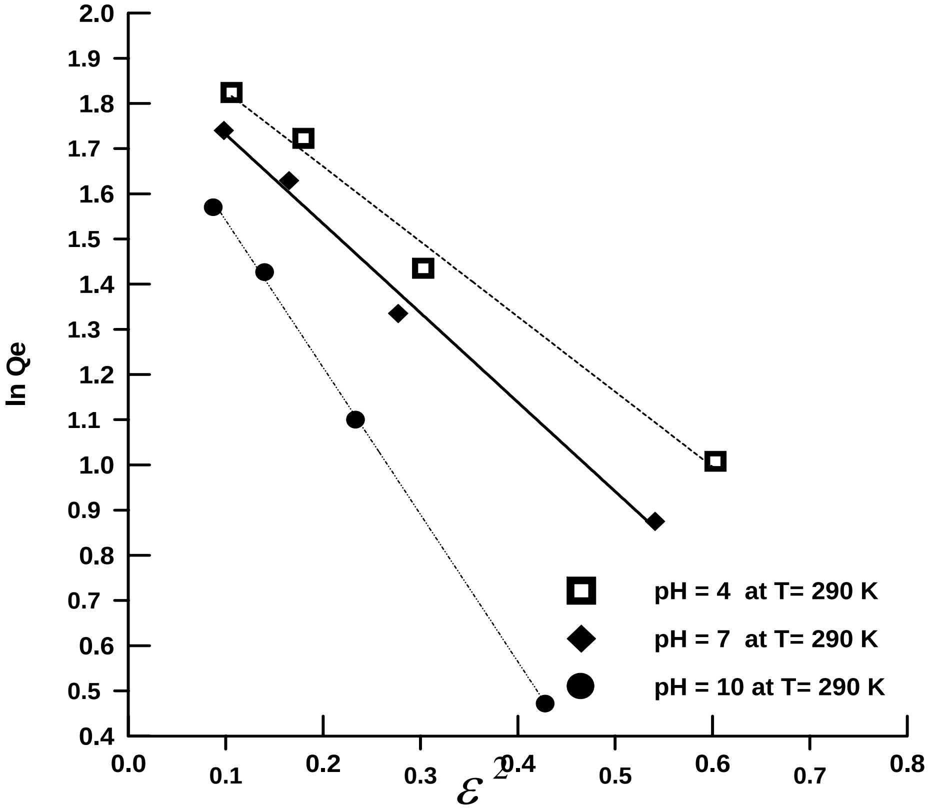

Figure 9: D-R plots Kaolinite / chromium tri-oxide (VI) at different pH$_S$.

Table 4. D-R isotherm parameters of the adsorption for chromium tri-oxide (VI) at different PHs, and temperatures on kaolinite surface.

Temp (K)	**pH**	**D-R isotherm parameters**			
		X_m ($mg.gm^{-1}$)	**K_m ($mole^2\ kJ^{-2}$)**	**E ($kJ\ mole^{-1}$)**	R^2
290	**4**	**1.992**	1.66065	0.5487	0.9896
300	**4**	**2.001**	1.99557	0.5005	0.9996
310	**4**	**1.967**	2.2144	0.4751	0.9983
290	**7**	**1.928**	1.97416	0.50328	0.9931
290	**10**	**1.866**	3.25347	0.39202	0.9994

Conclusion:

Kaolinite as an adsorbent has a considerable potential for removing chromium tri-oxide (VI), from aqueous solution due to its higher surface area.

As can be also understood from the present work, adsorbent amount of chromium tri-oxide decreased with increased pH and temperature.

The experimental data correlated reasonably well with the Freundlich and Dubinin _ Radushkevich D-R, but not with Langmuir, all parameters of these equations isotherms were calculated.

The order of heat of adsorption corresponds to a physical reaction and proved from D-R and Freundlich equations.

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