A study of Adsorption of Crystal Violet from Aqueous Solution on Kaolin

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Abstract

This study is concerned with the adsorption of Crystal violet from solution on the surface of kaolin. UV-spectrophotometric technique has been used to produce quantitative adsorption data at different conditions of contact time, ionic strength, pH and temperature.

The calculated data were in accordance with Freundlich equation and the adsorption isotherms are of S-curve type according to Giles classification. The results obtained show that adsorption process follows the first order rate expression.

The adsorption phenomenon was examined as a function of temperature (20, 30, 55 ^{o}C). The extent of adsorption of Crystal violet on the Kaolin was found to increase with increasing temperature (endothermic process). The basic thermodynamic functions have also been calculated.

The amount of dye adsorbed on the clay at different pH values showed an increase in the following order pH 7< 8.1<10.5<11.9.

The adsorption process is affected by the electrolyte concentration. The results indicated an decrease in adsorption of crystal violet in the presence of sodium hydrochloride.

الخلاصة:

يعنى هذا البحث بدراسة أمتزاز صبغة البلورات البنفسجية من محاولة المائي على سطح الكاؤولين الموجود بكثرة في الأراضي العراقية، وكان الغرض من الدراسة هو البحث عن أفضل الظروف الواجب توفرها في عملية تنقية المياه .وقد تم استخدام تقنية مطيافية الأشعة فوق البنفسجية لمعرفة كميات الامتزاز عند ظروف متباينة من الأس الهيدروجيني ودرجة الحرارة والقوة الأيونية لمحاول الامتزاز.

أظهرت النتائج أن ايزوثيرم الامتزاز من نوع (S) طبقا لتصنيف Giles والذي يتفق مع معادلة فرندلش للامتزاز، كما بينت النتائج بان أمتزاز صبغة البلورات البنفسجية يزداد بزيادة تركيز المادة الممتزة وان عملية الامتزاز تتبع قانون السرعة من المرتبة الأولى.

بينت الدراسة إن أمتزاز الصبغة على سطح الكاؤولين عند ثلاث درجات حرارية (20, 30, 55 ^{o}C) يزداد مع زيادة درجة الحرارة أمتزاز ماص للحرارة كما حسبت القيم الثرموديناميكية الأساسية لعملية الامتزاز.

وجد ان كمية أمتزاز الصبغة على سطح الكاؤولين عند قيم مختلفة من الأس الهيدروجيني يزداد وفقاً للترتيب الآتي:

7< 8.1<10.5<11.9

إن أمتزاز صبغة البلورات البنفسجية يتأثر بالقوة الأيونية للمحلول .فقد قلت كمية الصبغة الممتزة في المحلول بوجود كلوريد الصوديوم.

Introduction

Adsorption is physicochemical process which offers great potential as a mean of producing quality effluent. The study of adsorption is important for various physico-chemical processes and for understanding of phenomena such as clarification and depolution of industrial liquid (1). Adsorption applications have expanded rapidly due to sharp rising of environmental and quality requirements. It is often used as a method for treating aqueous solution to remove dissolved contaminating organic compounds which are highly toxic (2). Organic dyes are annually produced in huge quantities world wide. Most of these dyes are used in textile industry (3). Textile effluents are highly colored and their discharge into rivers makes water unfit for domestic, agricultural and industrial ourposes. The environmental behaviour of dyes is largely unknown (4), their long-term effects on animal and human health are not documented, with an exception of few studies (5). The de-colorization of textile industry wastewater is a world wide problem to which several successful treatment technologies have been applied, including adsorption and oxidation. The oxidation methods are effective only in waste water with a very low concentration of organic color. The adsorption process, by activated carbon and polymer resin (6-9), is relatively expensive, so the economic removal of dyes from waste water still remains a problem. Consequently, new adsorbents such as agricultural residues(10,11) and clays (12) are being studied.

The Aim of Present Work:

The aim of this work into investigates the capability of kaolin clay for the removal of crystal violet from wastewaters in different conditions of temperature, pH, ionic strength, and to calculate the thermodynamic functions at equilibrium conditions.

Materials and Methods

Instruments:

1- Visible spectrophotometer.
2- Dunboff metabolic shaking Incubater GCA/ precision Scientific.
3- Hettich Universal (D-7200), Centrifuge tubes.
4- Electronic Balance, Sartorius Lab. L420 B, ±0.0001.

Materials:

Crystal violet and sodium chloride were supplied by Fluka. Kaolin was obtained from "The General Company for Geological survey and mining".

Methodology

The clay was washed with excessive amounts of distilled water, dried at 160^{o}C for three hour. The clay was ground and sieved to a particle size of 75 μm.Wavelength of maximum absorbency ($\square_{max}$) was recorded for Crystal violet dissolved in aqueous media and found 590nm.

This value was utilized for estimation of quantity of dye adsorbed. Solutions of different concentrations were prepared by serial dilution at 590nm and plotted against concentration values. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Adsorption Isotherm

Solutions of crystal violet (5ml) of known concentrations (1.0□ 10^{-4}-15□ 10^{-4} M) at pH $\approx$10 were added to stoppered flasks containing 0.1g of kaolin. The flasks were shaken in a thermostatically controlled water bath at a speed of 60 cycle/min. till equilibrium is attained (30 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were centrifuged at 3000 rpm for 10 min. The clear supernatants were assayed for Crystal Violet spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of crystal violet adsorbed was calculated according to the following equation (13):-

$$Q_e \text{ or } \frac{x}{m} = \frac{V\,(C_o - C_e)}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1)}$$

Where:

x : the quantity adsorbed.

m : weight of adsorbent (g).

C_o : initial concentration (mg/L).

C_e : equilibrium concentration (mg/ L).

V : volume of solution (L).

Effect of Contact Time

Adsorption kinetic study was carried out by adding known amount of kaolin into 5ml dye solutions (15□ 10^{-4} M). The solutions were centrifuged at a desired time intervals and the residual dye concentration was determined.

Effect of Temperature

Adsorption experiment was repeated in the same manner at temperatures of 20, 30 and 55^{0}C to estimate the basic thermodynamic functions.

Effect of Ionic Strength

The effect of (0.154, 0.2 and 0.4M) sodium chloride solutions containing different concentrations of crystal violet in electrolyte solution were added to flasks containing 0.1 gm of kaolin. The procedure described for the adsorption experiment was followed.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of crystal violet. Buffer solutions were used to adjust the pH range from 7.0 to 11.9. The pH of the suspensions at the commencement of the adsorption was measured as well as at the end of experiment using pH-meter.

Results and Discussion

Adsorption Isotherm of Crystal Violet:

The adsorption of Crystal violet from aqueous solution on kaolin has been studied at temperature (30˚C) and at other two temperatures (20 and 55˚C) at pH ≈ 10.

The general shapes of crystal violet adsorption isotherms are shown in Figure (1), where the quantities adsorbed on Kaolin are plotted as a function of equilibrium concentration at the constant temperature.

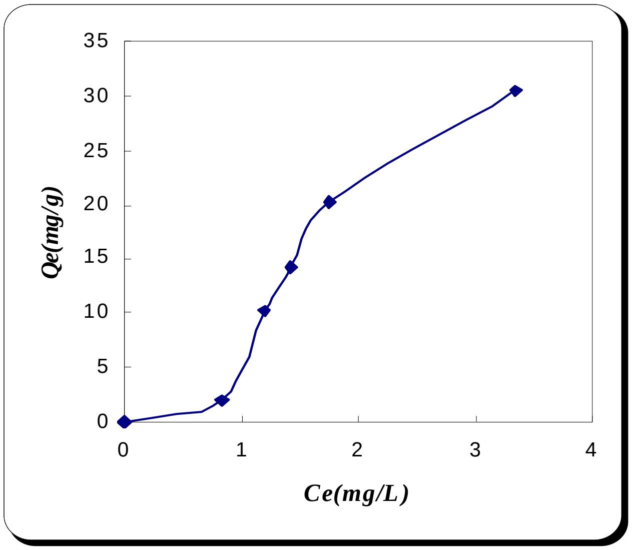

Figure (1) Adsorption isotherm of Crystal violet on kaolin at pH □ 10 and constant temperature (30 °C)

The results showed an increase in adsorptive capacities of kaolin as the concentration of crystal violet increased. Kaolin was found of reasonable surface activity in adsorption from solution of some materials and dyes (12,14).

the adsorptive capacity of kaolin has been attributed to electrostatic charges which may arise by two different mechanisms. Grim (15) has suggested that such charges may arise from broken bonds at the edge of the kaolin particle. Charges in the tetrahedral silicon layer will invariably be positive, irrespective of pH, while those in the octahedral aluminium layer will vary with pH. Being positive at low pH and negative at higher pH values. Thus at low pH, the entire edge carries a positive charge which will become less positive (and may even become negative) as the pH increases.

The shapes of Crystal violet adsorption isotherms were found to coincide with the S-type isotherm reported by Giles *et al.* (16).

The S-type isotherm depends upon the Freundlich assumption about the heterogeneity of the surface. The presence of various planes, as fibers leads to heterogeneous adsorption behaviour. Heterogeneity is a usual and a general feature of surface properties due to different unsaturated adsorption sites of different energetic behaviour (17).

The equilibrium adsorption of crystal violet on kaolin can be mathematically expressed in terms of adsorption isotherm. Adsorption isotherm data are best represented by applying the Freundlich equation.

$$\frac{x}{m} = kC_e^{1/n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathbf{2})$$

Where: $\frac{x}{m}$ is the quantity adsorbed in mg/g. C_e is the equilibrium concentration in mg/L, n and k are constants for the given adsorbent and solute.

The applicability of Freundlich isotherm is indicated by using the linear from of Freundlich equation.

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C_e \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathbf{3})$$

Figure (2) shows the linear relationship of *log Qe* versus *log Ce*. The values of Freundlich constants as well as the correlation coefficient are presented in Table (1). The fit of the data to the Freundlich model indicate that the forces of adsorption by polyester are governed by physisorption. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent-adsorbate system.

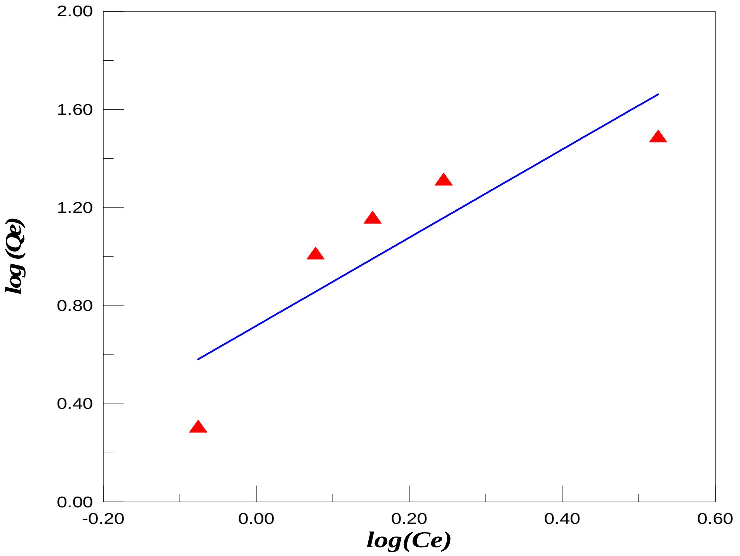

Figure (2): Linear form of Freundlich isotherm of crystal violet on kaolin

Table (1) Freundlich constants for the adsorption of crystal violet on kaolin

Adsorbate	**Kaolin**		
	n	K_f	**r**
Crystal violet	0.5566	0.1914	0.7810

The general shapes of crystal violet adsorption isotherms at three different temperatures are given in Figure (3).

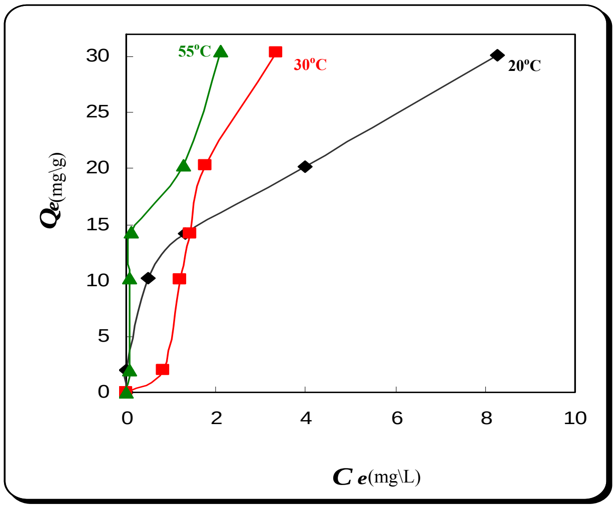

Figure (3): Adsorption isotherms of crystal violet on kaolin at pH □ 10 and different temperatures (°C)

The results showed a slight increase in the amount of dye adsorbed on kaolin with increasing temperature; hence the adsorption process appeared endothermic. The extent of adsorption of some dyes was found to increase with increasing temperature (18). This means the interaction between polyester and the dye molecules requires an appreciable energy in order to take place. Endothermic dye uptake can also be attributed to the possibility of occurring absorption or sorption process by the surface (19).

The basic thermodynamic quantities of adsorption of crystal violet on polyester were estimated through calculating Xm values at different temperatures. The heat of adsorption (ΔH) may be obtained from Van't Hoff equation: $\ln X_m = \frac{-\Delta H}{RT} +$ constant, the change in free energy (ΔG) could be determined from equation ($\Delta G = -RT\ln K$) and the change in entropy (ΔS) was calculated from Gibbs equation:($\Delta G = \Delta H - T.\Delta S$). Table (2) and Figure (4) demonstrate these calculations.

Table (2) Effect of temperature on the maximum adsorbed quantity for adsorption of crystal violet on kaolin

Adsorbate			Kaolin	
	T (k)	$10^3/T$ (k^{-1})	X_m (mg/g)	$\ln(X_m)$
			Ce= 2.25	
Crystal violet	293	3.356	31	3.434
	303	3.356	23	3.135
	328	3.145	16	2.772

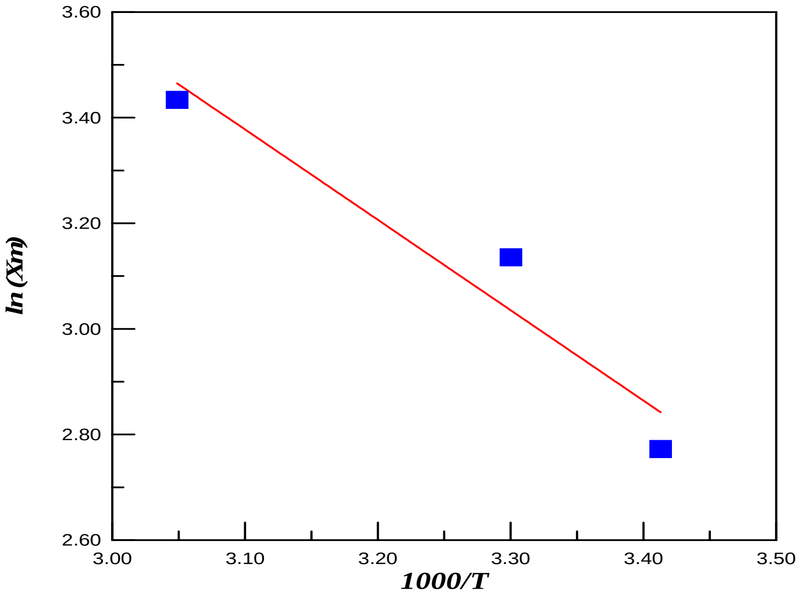

Figure (4): Plot of ln X_m against reciprocal absolute temperature for adsorption of crystal violet on kaolin

Table (3) shows the basic thermodynamic values of adsorption of crystal violet on kaolin. An adsorption of van der Waals type is suggested to take place as indicated by these values.

Table (3): Values of thermodynamic functions of adsorption process of crystal violet on Kaolin at *30 ^oC*

Adsorbate	Kaolin		
	ΔH kJ.mol^{-1}	ΔS J.mol^{-1}.k^{-1}	ΔG kJ.mol^{-1}
Crystal violet	+14.216	+44.279	-13.402

The adsorption of crystal violet on kaolin is endothermic and spontaneous as indicated by the positive value of enthalpy (ΔH) and negative value of free energy change (□G). The adsorption of crystal violet on kaolin is endothermic in conjunction with an increase in entropy.

The results obtained from the adsorption of crystal violet on clay showed an increase in adsorption quantities of the dye with increasing pH value (Figure (5)).

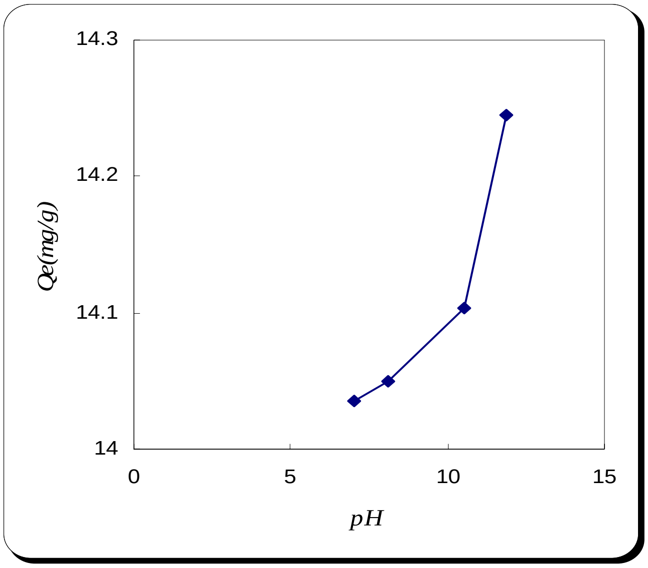

Figure (5) Effect of pH in adsorption uptake of crystal violet on kaolin clays at 30 ^{o}C

In the pH range studied, the molecular from of crystal violet is an ion bearing one positive charge (20), which suggests attachment to a negative site on the kaolin particle. The increase in the amount of adsorption with pH may then be due to two factors (12).

(i) An increase in the density of the negative charge on the edge of the kaolin due to the charge on the aluminium atoms at the edge changing from positive to negative.

(ii) The increased concentration of sodium hydroxide in the system needed to achieve high pH values replacement on the exterior of the clay lattice of the charge compensating cations of magnesium and calcium, by sodium ions. The resulting electrical imbalance in the clay lattice increases the negative charge on the particle as a whole and consequently favours the adsorption of a positively charged ion such as crystal violet.

The effect of ionic strength on adsorption uptake of crystal violet on kaolin was studied at variable concentrations of sodium chloride (0.154, 0.2 and 0.4M). Figure (6) shows the effect of ionic strength on the adsorption uptake of crystal violet on kaolin.

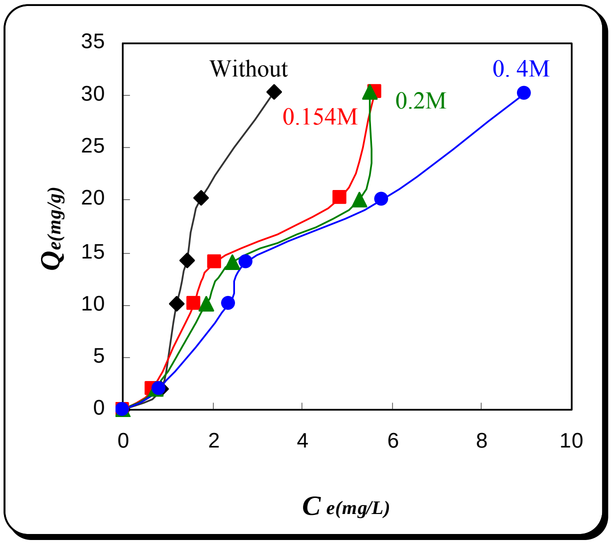

Figure (6) Adsorption isotherms of crystal violet on kaolin in the presence of different concentrations of sodium chloride at 30 °C

The adsorption extent has decreased on kaolin in the presence of electrolyte.

The solubility of crystals violet increases in the presence of various salts. When electrolytes are added, the precipitate formed of dye is capable of undergoing dispersion in pure water(13), therefore the decrease in adsorption uptake of the dye in the presence of 0.154 M NaCl and different concentrations of sodium chloride could be attributed to the increase in solubility and hence decrease the adsorption affinity towards the clay surface.

Adsorption Dynamics

Adsorption rate constant

Figure (7) shows the amount of dye adsorbed by kaolin as a function of time. The saturation curve rise sharply in the initial stage, indicating that there are plenty of readily accessible sites.

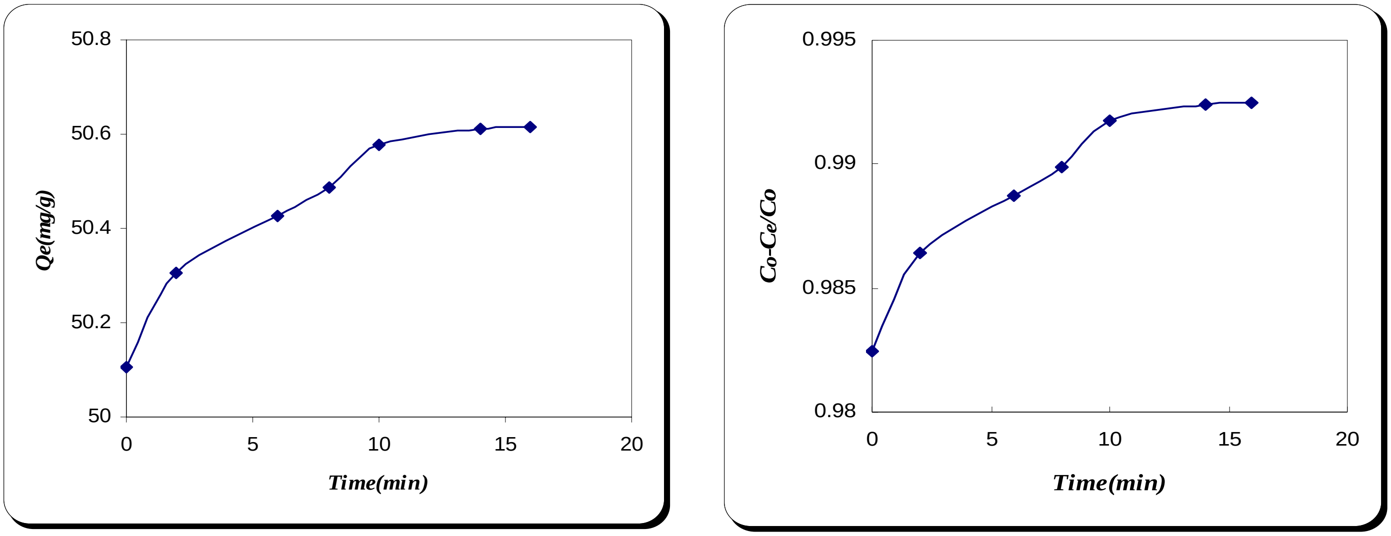

Figure (7) a- Adsorption kinetics of crystal violet – Kaolin system. b- Effect of contact time.

Adsorption rate constant (k_{ad}) is determined using Lagergren first order rate equation (21).

$$\ln (q_e-q_t) = \ln q_e - k_{ad}\, t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where q_e and q_t are adsorption densities (mg dye/gm of adsorbent) at saturation and at time t (min), respectively. Value of k_{ad} was obtained from the slope of the plot of $\ln (q_e-q_t)$ vs t (Figure (8)). The k_{ad} value for the adsorption of crystal violet on kaolin was reported to be 0.3424 min^{-1}.

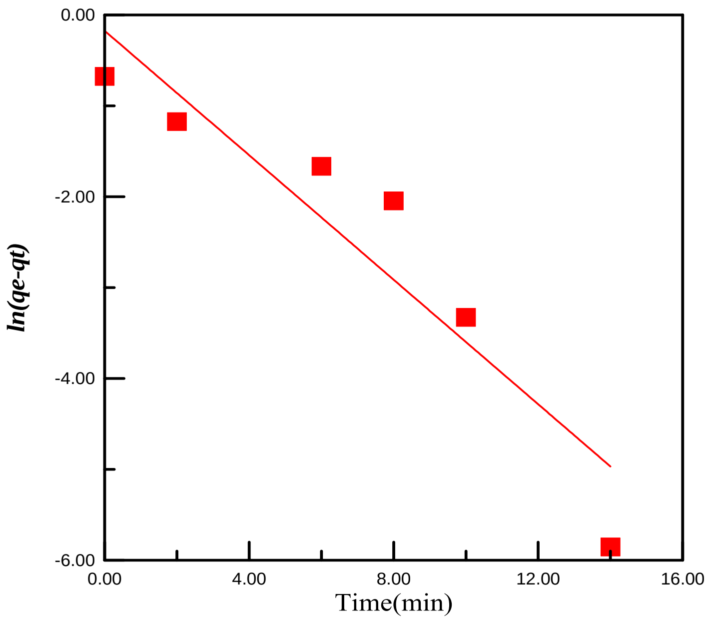

Figure (8): plot of **ln (q_e-q_t)** versus **t**

Conclusions

1. Kaolin surface appeared of high activity in the adsorption from solution of crystal violet.
2. The adsorption isotherms of crystal violet on Kaolin obeyed Freundlich isotherm.
3. Crystal violet-Kaolin reaction exhibited low enthalpy value (endothermic).
4. Adsorption of the dye on the clay was pH dependent.
5. There was a negative correlation between the amounts of crystal violet adsorbed and the ionic strength of solution.
6. The adsorption of crystal violet follows first-order kinetic.

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