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

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Abstract

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

The adsorption isotherms are of ***S-curve*** type according to Giles classification. Adsorption follows the first order rate expression and Freundlich isotherm n value was found to be 2.22, representing favorable adsorption.

The adsorption phenomenon was examined as a function of temperature ***(10, 25, 30 ^{o}C)***. The extent of adsorption of Crystal violet on the Polyester was found to increase with increasing temperature (***endothermic process***). The basic thermodynamic functions have also been calculated.

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

Introduction

Adsorption is an important surface phenomenon usually describes the accumulation of ions, atoms or molecules on a surface(1).It is a physicochemical process which offers great potential as a mean of producing quality effluent.This phenomenon of adsorpsion is basically due to the presence of residual forces at the sarface of a liquid or a solid. Adsorption is a spontaneous process and hence is attained by a decrease in free energy change and entropy of the system. The concept of adsorption equilibrium is involved deeply in the measurment and correlation of adsorption capacity, selectivity and regenerability data. Generally, equilibrium is the constraint that limits each of these vital factors for adsorption application. However, there are many phenomena where adsorption is essential to the process such as decolorisation and dyeing of fibers, these processes occcur through the adsorption process on solid surfaces(such as activated charcoal, clays and fibers)(2-5). In the process of dyeing, a complication sometimes arises which is not normally found with other adsorbents (6). The studies of adsorption by fibers has recently become the subject of considerable interest. There are reports on the adsorption of dyes by cotton texitile (7,8), natural cellulose (9,10) and acrylonitral (11).

The Aim of Present Work:

The aim of this work into investigate the factors affecting the dyeing of polyester by crystal violet, 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, $\pm$0.0001.
5- pH-Meter, HM-73, TDA Electronic Ltd.

Materials:

Crystal violet and sodium chloride were supplied by Fluka. Polyester was obtained from "Al-diwaniya textile factory".

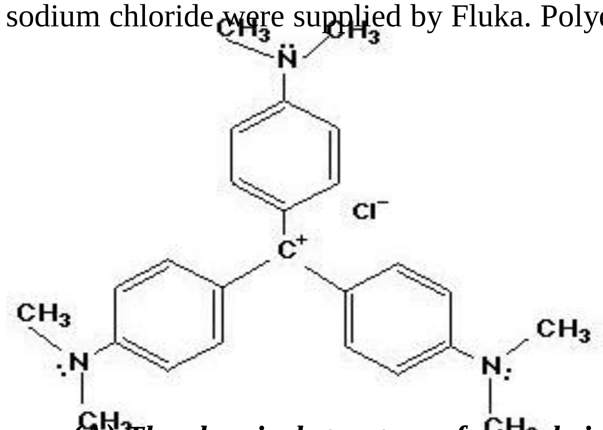
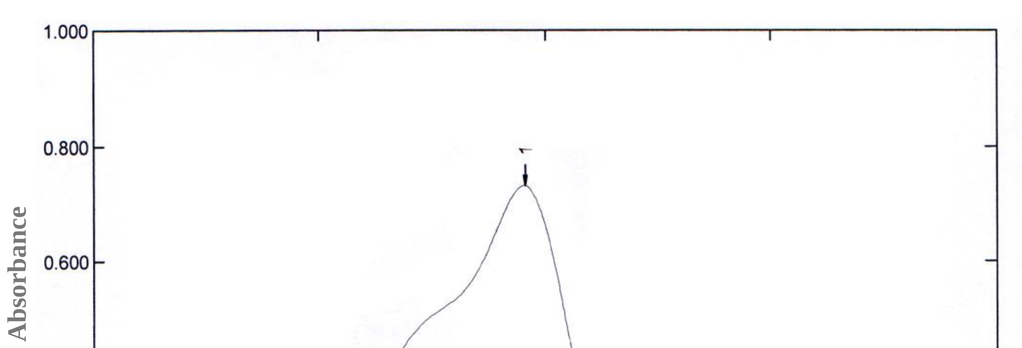


Figure (A) The chemical structure of crystal violet

Methodology

Polyester was washed with excessive amounts of distilled water, dried at 80^{o}C for one hour. Wavelength of maximum absorbency (λ_{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

The adsorption isotherms were determined by shaking 0.12g of polyester into 10ml dye solutions, having concentrations ranging from $5x10^{-6}$ - $4x10^{-5}$M at pH$\approx$10. After 60min. of shaking, the suspensions were centrifuged at 3000 rpm for 10 min. The dye concentration was determined spectrophotometrically.

The quantity of crystal violet adsorbed was calculated according to the following equation (12):-

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

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 (0.12gm) of polyester into 10ml dye solutions ($1x10^{-5}$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 10, 25 and 30^0C to estimate the basic thermodynamic functions.

Effect of Ionic Strength

The effect of (0.154, 0.25 and 0.4M) sodium chloride solutions containing different concentrations of crystal violet in electrolyte solution were added to flasks containing 0.12 gm of polyester. The procedure described for the adsorption experiment was followed.

Results and Discussion

Adsorption Isotherm of Crystal Violet:

The adsorption of Crystal violet from aqueous solution on polyester has been studied at temperature (10˚C) and at other two temperatures (25 and 30˚C) at pH ≈10.

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

The results showed an increase in adsorptive capacities of polyester as the concentration of crystal violet increased.

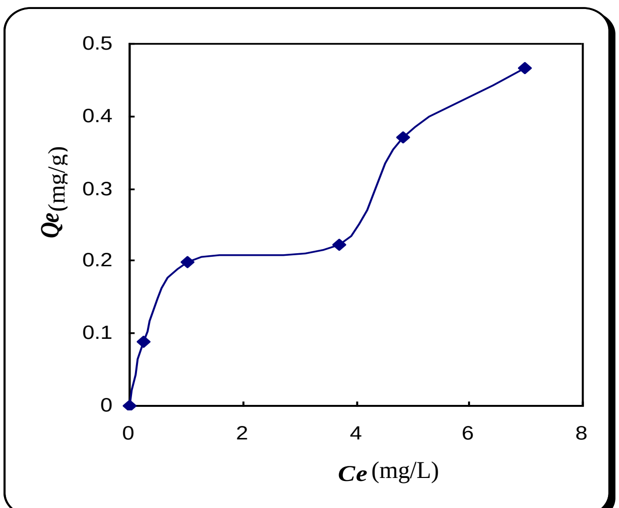


Figure (1) Adsorption isotherms of Crystal violet on polyester at pH ≈10 and constant temperature (10 ^{o}C)

The shapes of Crystal violet adsorption isotherms were found to coincide with the S_4-type isotherm reported by Giles *et al.* (13).

The S_4-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 (14).

The adsorption of crystal violet on Polyester, follow isotherms which are best represented by applying the Freundlich equation.

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

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.

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

Figure (2) show 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 correlation coefficient close to 1 indicates that the adsorption process conforms to Freundlich isotherm. 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.

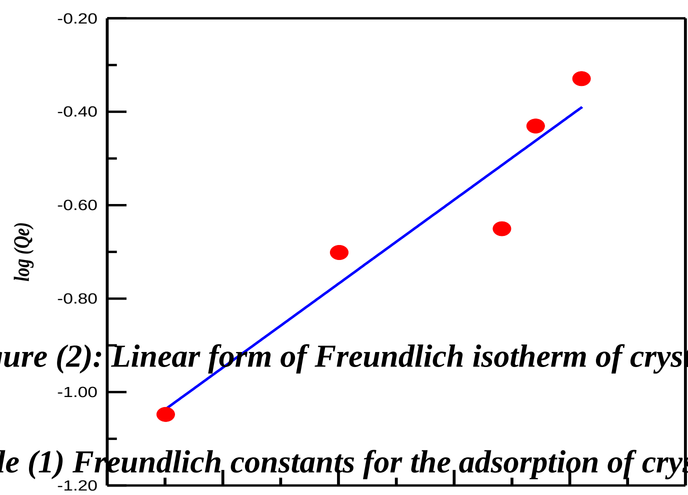


Figure (2): Linear form of Freundlich isotherm of crystal violet on polyester

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

n	K_f	r
2.2287	0.1706	0.9107

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

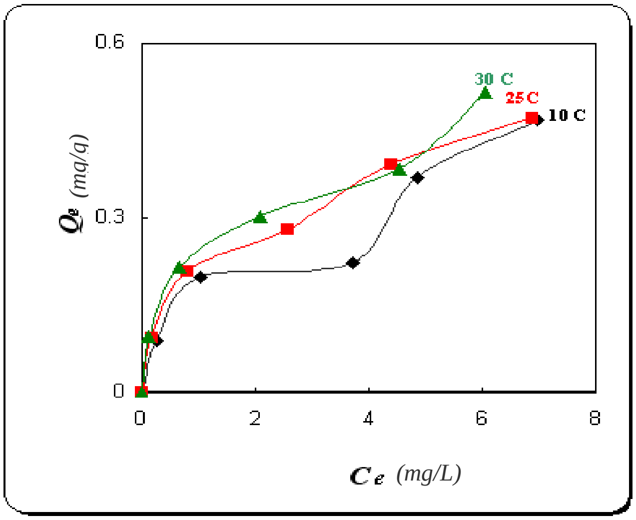


Figure (3): Adsorption isotherms of crystal violet on polyester at pH ≈10 and different temperatures (^oC)

The results showed a slight increase in the amount of dye adsorbed on polyester with increasing temperature; hence the adsorption process appeared endothermic. The extent of adsorption of some dyes was found to increase with increasing temperature (15). 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 (16). The fibers may be swollen by the solvent to the extent that they can be penetrated by both solvent and dye (17).

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:

$$\ln X_m = \frac{-\Delta H}{RT} + \text{constant},$$

the change in free energy (ΔG) could be determined from equation (ΔG = –RTlnK) 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 polyester

***T* (k)**	**10^3/*T* (*k^{-1}*)**	***X_m* (mg/g)**	***$ln(X_m)$***
		***Ce*= 2.1**	
283	3.534	0.205	-1.585
298	3.356	0.254	-1.370

Table (3) shows the basic thermodynamic values of adsorption of crystal violet on polyester. 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 Polyester at 30 ^oC

Adsorbate	Polyester		
	ΔH kJ.mol^{-1}	***ΔS J.mol^{-1}.k^{-1}***	***ΔG kJ.mol^{-1}***
Crystal violet	7.939	30.626	-1.340

The negative value of ΔG indicates the feasibility of the process and also the spontaneity of adsorption reaction. The value of enthalpy (ΔH) is positive and it confirms the endothermic character of the reaction. The positive value of entropy shows the increased randomness at the solid-solution interface during the adsorption of crystal violet on polyester.

The effect of ionic strength on adsorption uptake of crystal violet on polyester was studied at variable concentrations of sodium chloride (0.154, 0.25 and 0.4M). Figure (5) shows the effect of ionic strength on the adsorption uptake of crystal violet on polyester.

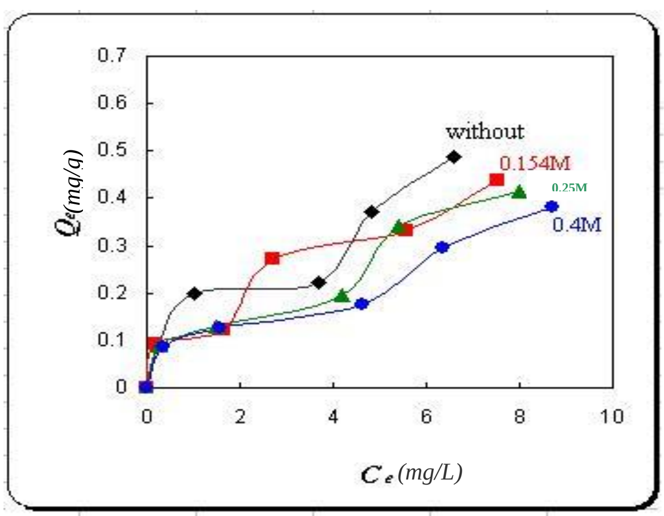


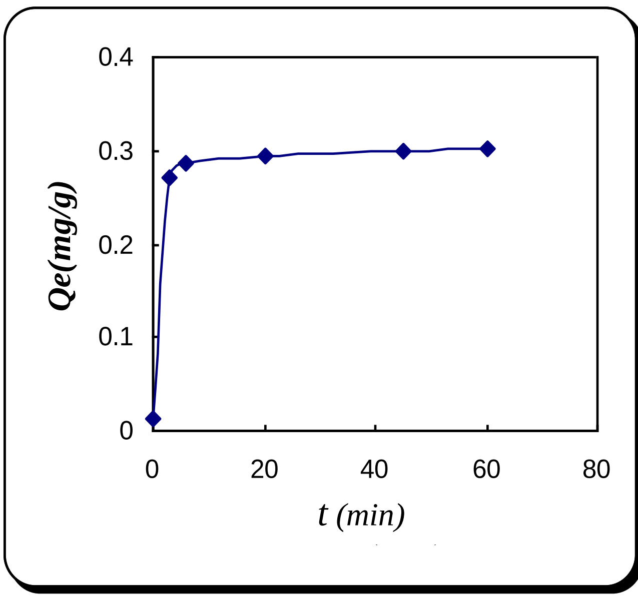
Figure (5) Adsorption isotherms of crystal violet on polyester in the presence of different concentrations of sodium chloride

The adsorption extent has decreased on polyester in the presence of electrolyte. The solubility of dye increases in the presence of salts. When electrolytes are added, the precipitate formed of dye is capable of undergoing dispersion in pure water (18), therefore the decrease in adsorption uptake of crystal violet 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 (6) shows the amount of dye adsorbed by polyester as a function of time. The saturation curve rise sharply in the initial stage, indicating that there are plenty of readily accessible sites.Eventually, a plateau is reached in curve indicating that the adsorbent is saturated at this level. The equilibrium time was found to be 60 min.



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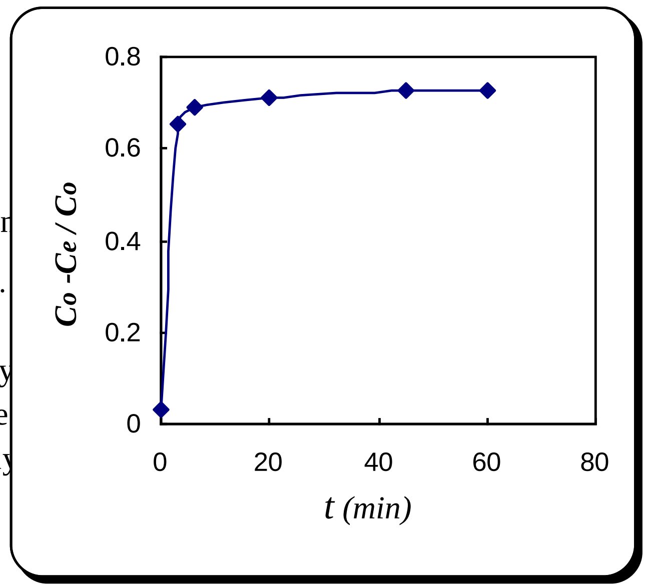

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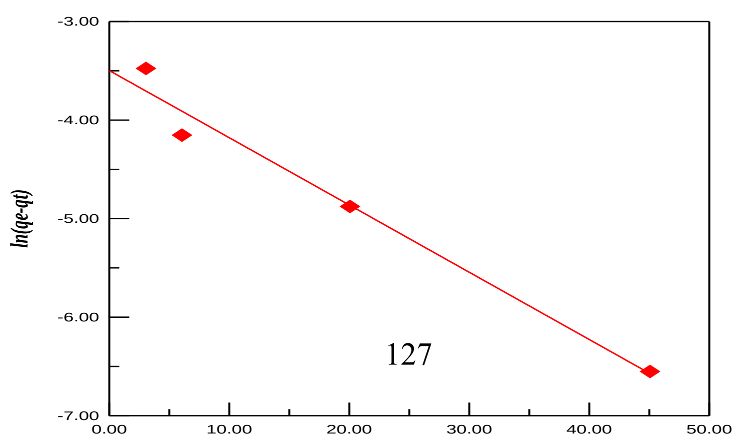
Figure (8) a- Adsorption kinetics of crystal violet – polyester system. b- Effect of contact time.



CONCLUSIONS:

1. Polyester surface appeared of high activity in the adsorption from solution of crystal violet.
2. The adsorption isotherms of crystal violet on Polyester obeyed Freundlich isotherm.
3. Thermodynamic parameters show that the adsorption process is endothermic and spontaneous, which implies increased sorption at higher temperatures.
4. There was a negative correlation between the amounts of crystal violet adsorbed and the ionic strength of solution.
5. The adsorption of crystal violet follows first-order kinetic.

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دراسة أمتزاز صبغة البلورات البنفسجية من محلولها المائي على سطح البولي أستر

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الخلاصة:

يعنى هذا البحث بدراسة أمتزاز صبغة البلورات البنفسجية من محلولها المائي على سطح البولي أستر المتوفر محليا، وكان الغرض من الدراسة هو البحث عن أفضل الظروف الواجب توفرها في عملية الصباغة بهذه الصبغة .وقد تم استخدام تقنية مطيافية الأشعة المرئية لمعرفة كميات الأمتزاز عند ظروف متباينة من زمن التماس ودرجة الحرارة والقوة الأيونية لمحلول الأمتزاز.

أظهرت النتائج أن أيزوثيرم الأمتزاز من نوع (***S***) طبقا لتصنيف ***Giles*** وإن عملية الأمتزاز تتبع قانون السرعة من المرتبة الأولى و أيزوثيرم فرندلش للأمتزاز حيث وجدت قيمة n تساوي 2.22 وتدل هذه القيمة على أفضلية حدوث عملية الأمتزاز.

بينت الدراسة إن أمتزاز الصبغة على سطح البولي أستر عند ثلاث درجات حرارية ***(10, 25, 30 ^{o}C)*** يزداد مع زيادة درجة الحرارة **أمتزاز ماص للحرارة** كما حسبت القيم الثرموديناميكية الأساسية لعملية الأمتزاز.

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