A Kinetics Study of Crystal Violet and Congo red Adsorption on Cellulose and Polyester Fibers

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Abstract

In this work, cellulose fibers and polyester as adsorbents for two dyes (crystal violet and congo red) in aqueous solutions were studied with kinetic adsorptions. The adsorption process of two dyes on cellulose fibers was reached complete equilibrium within 30min., while the adsorption of crystal violet and congo red on polyester was reached equilibrium after 60min. and 30min. respectively.

The maximum adsorption and the adsorption rate of crystal violet on cellulose are much higher than that of congo red. The inverse was true for the adsorption of dyes on polyester.

The kinetics of dyes adsorption has been studied in terms of pseudo-first order and pseudo-second order rate expression. The results indicated that adsorption process followed two models and demonstrated that intraparticle diffusion plays a significant role in the adsorption mechanism.

الخلاصة

يعنى هذا البحث بدراسة حركية أمتزاز صبغة البلورات البنفسجية وصبغة الكونغو الحمراء من محاليلها المائية على سطحي البولي أستر وألياف السليلوز المتوفرة محلياً، وكان الغرض من هذه الدراسة هو التعـرف على ميكانيكية عمليلة امتزاز هذه الصبغات على السطوح المذكورة أنفاً.

أن الزمن اللازم لحدوث الاتزان في عملية الامتزاز الصبغتين على سطوح الياف السليلوز هو 30 دقيقة ، بينما كان الزمن اللازم لحدوث عملية امتزاز صبغة البلورات البنفسجية والكونغو الحمراء على سطح البـولي أستر هو 60 دقيقة و30 دقيقة على التوالي.

بينت الدراسة أن كمية وسرعة أمتزاز صبغة البلورات البنفسجية على سطح الياف السليلوز كانت اكبـر مقارنة بأمتزاز صبغة الكونغو الحمراء على نفس السطح. والعكس صحيح بالنسبة لعملية امتزاز الصبغتين على سطح البولي استر.

أظهرت نتائج حركة الامتزاز بان عملية امتزاز الصبغتين على سطحي البولي استر والياف السليلوز تتبع قوانين السرعة من المرتبة الاولى والثانية وان الانتشار الضمني للدقائق يلعب دوراً رئيسياً في عملية الامتزاز.

Introduction

Major contaminants found in wastewater include biodegradable, volatile, and recalcitrant organic compounds; toxic metals; microbial pathogens; and parasites causing deterioration of the surrounding medium that can present a great danger to the environment and human health[1,2,3]. Several studies have been undertaken on the toxicity of dyes and their impact on ecosystems[4,5]. These studies show that certain dyes degrade and that their derived products can be toxic and carcinogenic even at law concentrations[5]. Biological treatment has been shown to be very efficient for the decrease of biological and chemical organic demand, but it is ineffective for the elimination of dyes from wastewater[6]. Several techniques such as ultrafiltration[7] oxidation by UV/H_2O_2[8], direct precipitation of the pollutants by membrane processes[9], and adsorption methods[10] have been studied. Adsorption has been extensively used in industrial processes for either separation or purification.

Most conventional adsorption plants use activated carbon, which is an expensive material. Besides, there is growing interest in using commercially available low-cost materials for the adsorption of dyes including fly ash[11], natural clays[12,13], wood chips[14], cotton[15], natural cellulose[16] and diatomaceous silica[17]. Identification of a potential dye sorbent must be in good agreement with its dye binding capacity, its regeneration properties, its requirements and limitation with respect to environmental conditions[18].

The Aim of Present Work:

The aim of this study was to evaluate the capacity of polyester and cellulose fibers to remove crystal violet and congo red dyes. Equilibrium and kinetic analysis were conducted to investigate the mechanism of dye adsorption and optimization of various parameters in dye recovery.

Materials and Methods

***Instruments*:**

1- Visible spectrophotometer.

2- Dunboff metabolic shaking Incubater GCA/ precision Scientific.

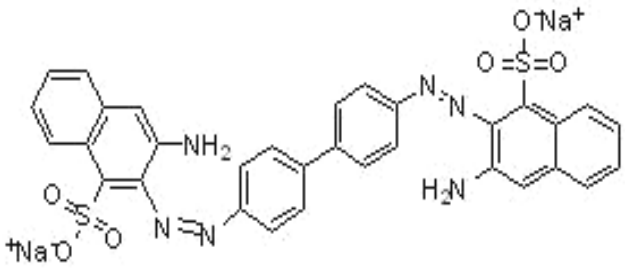
3- Centrifuge tubes. Hettich Universal (D-7200).

4- Electronic Balance, Sartorius Lab. L420 B, $\pm$0.0001.

5- pH-Meter, HM-73, TDA Electronic Ltd.

Materials:

Crystal violet, congo red and sodium chloride (Figure (A)) were supplied by Fluka. Polyester and cellulose fibers were obtained from "Al-diwaniya textile factory".



-a- **-b-**

Figure (A) The chemical structure of a- Congo Red b- Crystal Violet Methodology

Polyester was washed with excessive amounts of distilled water, dried at 80^{o}C for one hour. The cellulose surface was used without further treatment. Wavelength of maximum absorbancy (λ_{max}) for each dye was selected, and found 590nm for crystal violet and 495nm for congo red. These values were utilized for estimation of quantity of dyes adsorbed.

Solutions of different concentrations for each dye were prepared by serial dilution. Absorbance values of these solutions were measured at the selected λ_{max} value for each dye and plotted 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.

Calculate the quantity adsorbed

The quantities of dyes adsorbed were calculated according to the following equation[19]:-

Q_e *or* $\frac{x}{m} = \frac{V\,(C_o - C_e)}{m}$ …… (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).

Kinetic Studies

Effect of contact time was determined by adding 0.1gm of adsorbent into 10ml dye solution, with initial concentration ($1x10^{-5}$M or $3x10^{-5}$M), under shaking. The temperature of solution was held constant at 20^{0}C with a thermostatic shaker. After different time intervals, the solutions were centrifuged and volumes of 1ml supernatant were taken for spectrophotometrically measurements of dye content.

Results and Discussion

Adsorption rate constants of dyes on cellulose fibers

To determine the equilibrium time for the maximum uptake of dyes, the adsorption of crystal violet and congo red on cellulose fibers was studied as a function of contact time, and the results are shown in Figures (1) and (2). It can be concluded that the rates of dyes uptake on cellulose fibers are higher during the initial stages and gradually decrease and become almost constant after a period of 30min. for both dyes.

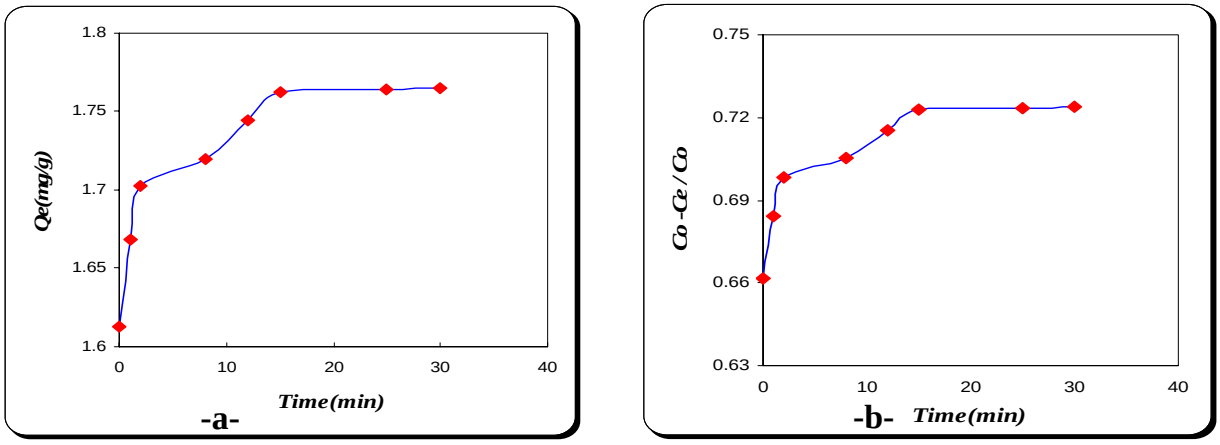


Figure (1) a- Adsorption kinetics of crystal violet-cellulose system
b- Effect of contact time

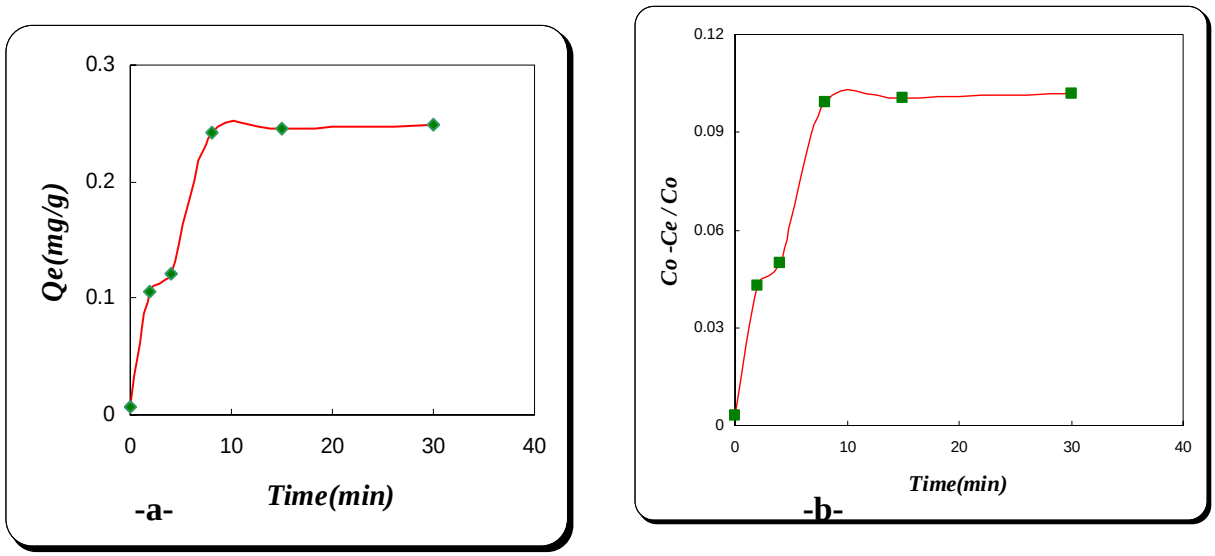


Figure (2) a- Adsorption kinetics of conge red-cellulose system
b- Effect of contact time

Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data. The rate constants of the dyes removal from the solution by cellulose were determined using first order and pseudo-second order equations.

The lagergren first order rate equation was used to fit the experimental results. The linear form the lagergren equation is[20]:

$$ln(q_e - q_t) = ln\, q_e - k_1\, t \quad \ldots\ldots(2)$$

Where q_e (mg/g) is the equilibrium sorption capacity and q_t (mg/g) is the amount of dye adsorbed at time t (min). Values of k_1 for crystal violet-cellulose and congo red-cellulose systems were obtained from the slope of

the plot of $ln(q_e-q_t)$ vs. t (Figure (3)). The adsorption kinetic parameters from Figure (3) are indicated in Table (1).

The adsorption data were also analyzed in terms of a pseudo-second order mechanism[21,22]. The linear form of the equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \left(\frac{1}{qe}\right)t \text{.....(3)}$$

Where k_2 (g.mg $^{-1}$.min) is the rate constant of the pseudo – second order adsorption.

If the initial adsorption rate is

$h = k_2 q_e^2$

Then equation (3) becomes.

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \text{.....(4)}$$

by plotting t/q_t versus t (Figure (4)), a straight line could be obtained and q_e, k_2 and h can be calculated. The adsorption kinetic parameters from Figure (4) are listed in Table (1).

Table (1) Adsorption kinetic parameters of dyes on cellulose fibers

	Pseudo-first order			***Pseudo-second order***			
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_1 (g. mg^{-1} .min^{-1})	q_e (mg/g)	R^2	h (mg. g^{-1} .min^{-1})
Crystal Violet	0.199	0.133	0.934	4.545	1.771	1.00	14.224
Congo Red	0.910	1.117	0.934	0.577	0.338	0.918	0.0658

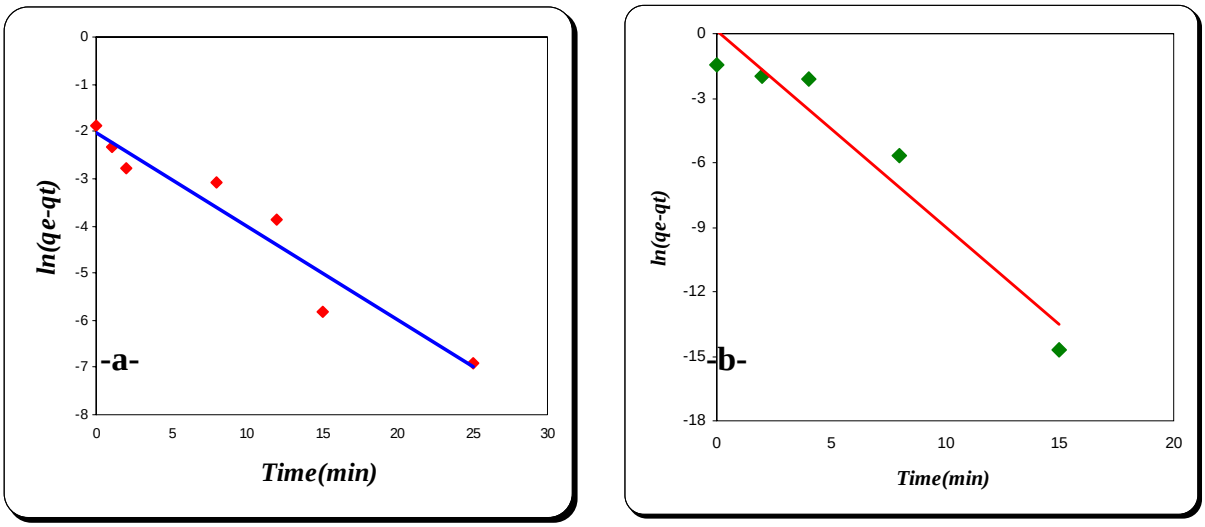


Figure (3) the applicability of the first order kinetic model to a) crystal violet and b) Congo red adsorption on cellulose fibers.

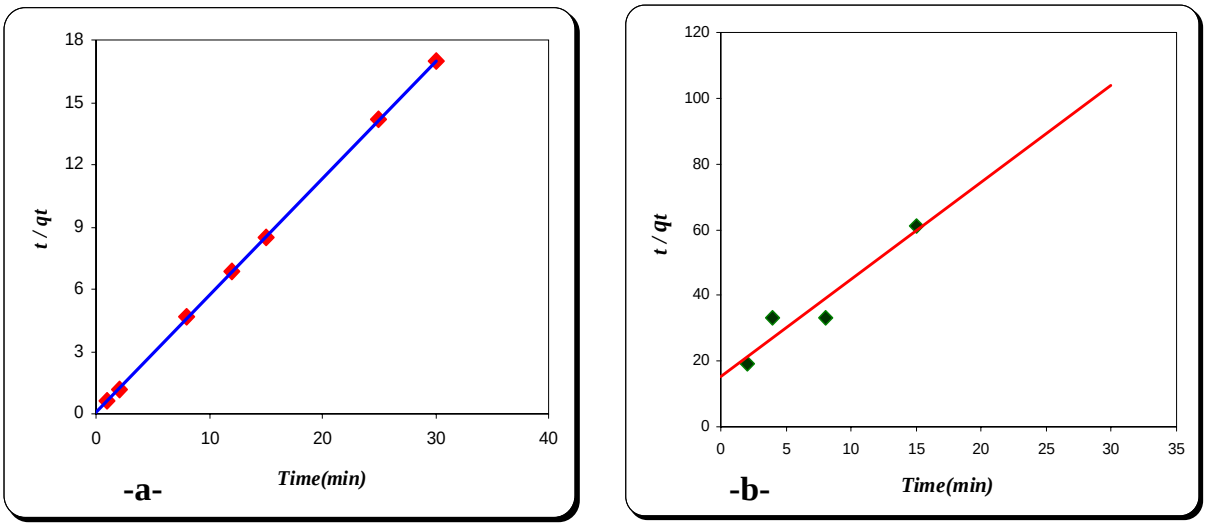


Figure (4) the applicability of the second order kinetic model to a) crystal violet and b) Congo red adsorption on cellulose fibers.

The applicability of the lagergren and pseudo-second order models can be examined by linear plots of $ln(q_e-q_t)$ vs. t and t/q_t vs. t, respectively as shown in Figures (3) and (4), respectively. To quantify the applicability of each model the correlation coefficient, R^2, was calculated from these plots. The correlation coefficient, R^2, show that the pseudo-second order model fits the experimental data slightly better than the pseudo-first order. This fact indicates that the intraparticle diffusion is the rate-controlling step.

The mechanism of dye adsorption on the textile materials, which may involve the following three steps: (*i*) diffusion of dye molecules through the solution to the surface of adsorbent; (*ii*) adsorption of dye molecules on the surface of the materials through the molecular interactions; (*iii*) diffusion of dye molecules from the surface into the interior of the adsorbent molecules. The second step of the adsorption of dyes on the materials is dependent on the nature of the dye molecules such as anionic or cationic structures[23]. Due to the negatively charged characteristics of cellulose in aqueous media, the cationic dye should be adsorbed more rapidly than anionic dye. The results obtained here indicate the effect of coulombic interactions between the adsorbent and dyes.

Adsorption rate constants of dyes on polyester fibers

The adsorption kinetic of crystal violet on polyester was reported previously[24] (Figure (5)). Figure (6) shows the amount of congo red adsorbed by polyester as a function of time. The dyes uptake versus time curves is single, smooth, and continuous leading to saturation, suggesting the possible monolayer coverage of the dye on the surface of the adsorbent[25].

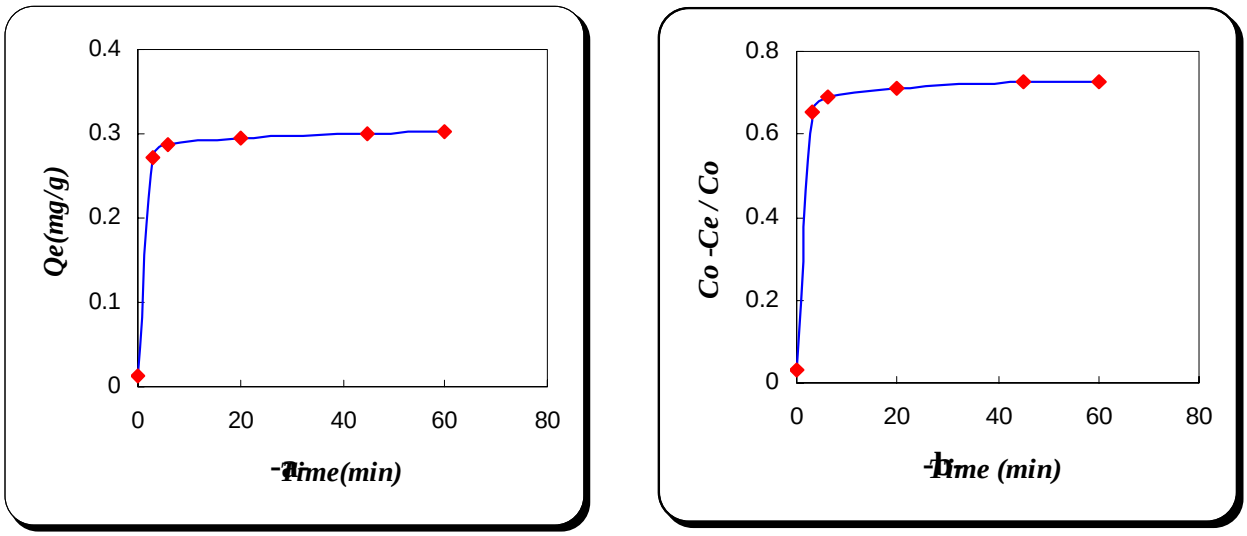


Figure (5) a- Adsorption kinetics of crystal violet-polyester system b- Effect of contact time

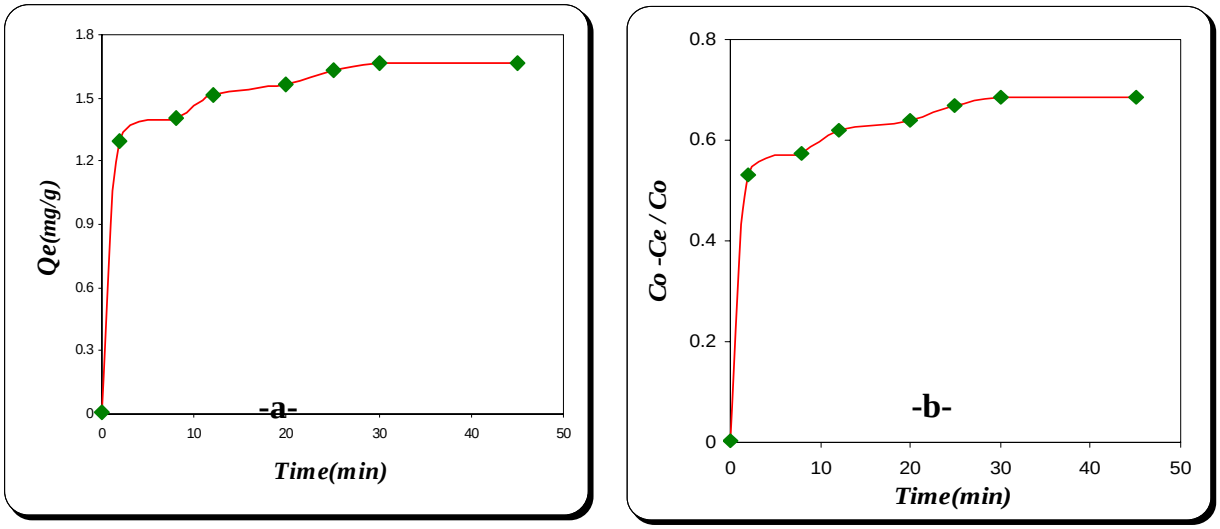


Figure (6) a- Adsorption kinetics of conge red-polyester system b- Effect of contact time

The experimental kinetic data were adjusted according to first-order kinetic (equation (3)) and to pseudo-second order kinetic (equation (2)). The linearity of the plots indicates the applicability of the two models (Figures (7) and (8)). The correlation coefficients as well as the kinetic parameters of dyes adsorption on polyester are given in Table (2).

The adsorption capacity of congo red is much higher than that of the crystal violet. The rate of adsorption of congo red on polyester was found to be greater than those for crystal violet.

Table (2) Adsorption kinetic parameters of dyes on polyester fibers

	Pseudo-first order			*Pseudo-second order*			
	k_1 [24] (min^{-1})	q_e (mg/g)	R^2	k_1 ($g.\ mg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	h ($mg.\ g^{-1}.min^{-1}$)
Crystal Violet	0.068	0.0302	0.978	8.219	0.302	1.00	0.749
Congo Red	0.122	0.842	0.878	0.642	1.692	0.99	1.838

The results of Table (2) showed that the second order equation model provided the best correlation with experimental results. It can be said that the adsorption process may involve more than one step, calling upon the transfer by a diffusion layer, or an interface of diffusion, and the intraparticle diffusion. The intraparticle diffusion step of the adsorption processes, which certainly should affect the adsorption of dyes on the substrates.

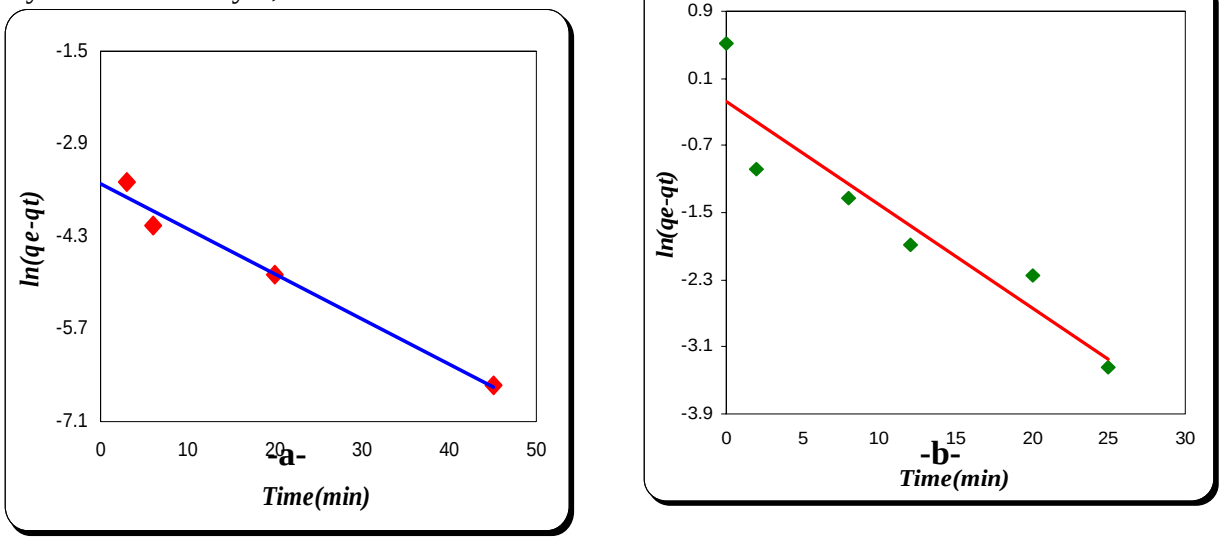


Figure (7) The applicability of the first order kinetic model to a) crystal violet and b) conge red adsorption on polyester

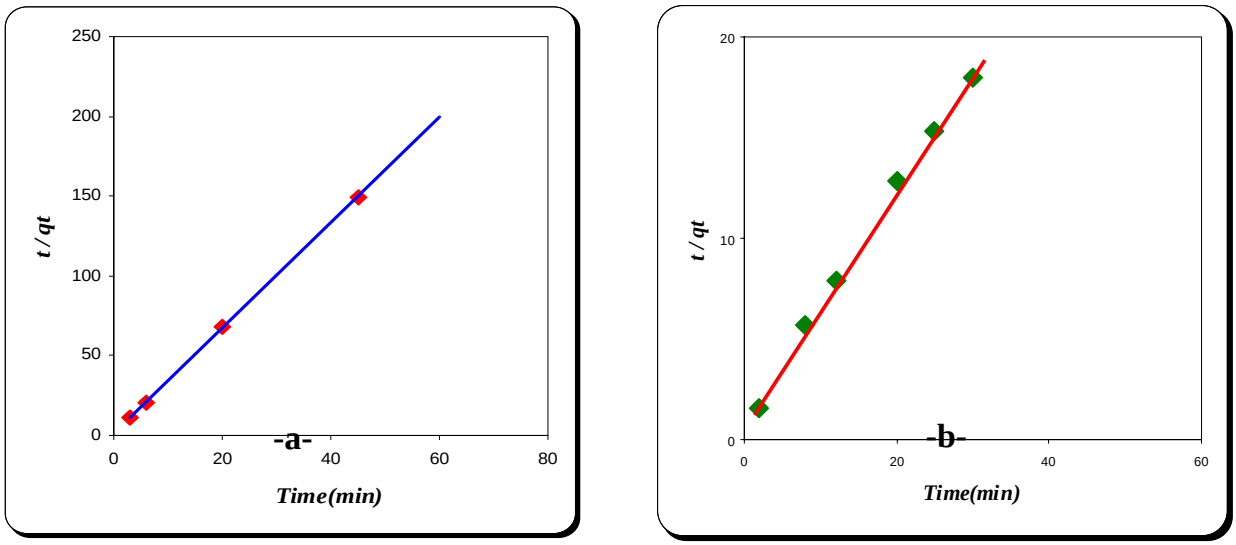


Figure (8) The applicability of the second order kinetic model to a) crystal violet and b) conge red adsorption on polyester

Conclusions

1. The cellulose fibers and polyester could be employed as adsorbents in wastewater treatment for the removal of crystal violet and congo red dyes.
2. The process of adsorption is relatively fast and the kinetic adsorption data fitted well to the second order kinetic model, indicating an intraparticle diffusion mechanism.

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