

Removal of Blue Dye From Wastewater by Adsorption onto Activated Carbon

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Abstract

The aim of the present work is the adsorption of the blue dye from wastewater onto activated carbon by using continuous system (fixed-activated carbon bed). Continuous adsorption experiments of fixed bed were carried out to study the effects of (flow rate Q , initial dye concentration C_0 , bed depth Z , and carbon particle size $P.S$) on the adsorption capacity and performance of fixed bed adsorber.

Adsorption through granular activated carbon was found to be very effective for the removal of the blue dye, where the percent dye removal was 90%.

The equilibrium data were determined experimentally and the equilibrium isotherm was found to be of a favorable type and fit well by Langmuir and Freundlich isotherms. The study was developed a multiple linear regression model between the independent variables (Q , C_0 , Z , $P.S$) and the dependent variables (Time t , Amount of adsorbate q) separately, the verification and the correlation coefficient (R) (0.92, and 0.95) for these correlation respectively, illustrate that the experimental data correlated well with the modeling data.

Batch process was carried out to obtain the surface diffusivity by comparing the experimental and theoretical results of the fractional uptake.

الخلاصة

الهدف من العمل التجريبي الحالي هو دراسة إمكانية إزالة الصبغة الزرقاء من مياه المخلفات من خلال عملية الامتزاز بالفحم المنشط بواسطة نظام مستمر الجريان لعمود امتزاز ذو حشوة ثابتة من حبيبات الفحم المنشط. تجارب النظام المستمر تم تنفيذها لدراسة تأثير متغيرات (معدل الجريان Q ، تركيز الصبغة الداخل C_0 ، سمك الحشوة Z ، وحجم حبيبات الفحم المنشط $P.S$) على سعة الامتزاز لعمود الامتزاز وتقييم ادائه. وقد وجد ان عملية الامتزاز بالفحم المنشط الحبيبي كانت فعالة في إزالة الصبغة الزرقاء، إذ وصلت نسبة الإزالة إلى 90%.

بيانات حالة التوازن حددت عمليا ولوحظ ان منحني التوازن الذي يمثل العلاقة بين تركيز التوازن وكمية الامتزاز (كغم مادة ممتزة / كغم كاربون)، هو من النوع المفضل ويتطابق مع معادلتى (لانكمير) و(فرنديلش). تم دراسة موديل الانحدار الخطي المتعدد بين المتغيرات المستقلة (Q , C_0 , Z , $P.S$) والمتغيرات المعتمدة (كمية المادة الممتزة q)، ووقت الامتزاز t) كل على حدة. ان عمل تحقيق لهذه العلاقات وإيجاد معامل الترابط (0.92، 0.94) للعلاقين على التوالي وضح ان القيم التجريبية مترابطة بشكل جيد مع القيم المحسوبة من معادلة الانحدار الخطي المتعدد.

نظام الدفعات تم تنفيذه للحصول على النفاذية السطحية من خلال مقارنة النتائج العملية والنظرية لنسبة المادة التي تم امتزازها.

Introduction

Adsorption onto solid can be defined as the phenomena that taking up the molecules from the fluid phase onto the solid surface. Adsorption is probably one of the most common advanced wastewater treatment processes, and it finding increased used in the wastewater treatment for removal of refractory toxic substances (Weber, 1972). Adsorption on activated carbon is used to any significant extent for the removal of dissolved organic from wastes and polluted waters (Weber, 1972).

Activated carbon is an effective adsorbent primarily due to its extensive porosity and very large available surface area for adsorption (Jason, 1999).

Liquid-solid adsorption onto activated carbon is characterized by slow rates and long periods between actions. The liquid flowing through an adsorber may be in

contact with the carbon for a few minutes, such as when removing taste from water, or for several hours, as in the case of decolorizing sugar solution. The granular carbon life may extend from a few days, for sugar solutions, to several years for taste removal (Erskine, 1971).

The driving force of mass transfer solute from solvent to on the surface of solid adsorption may be the lyophobic (i.e. solvent- rejecting) character of the solute or the affinity of the solute for the solid or combination of both.

Batch processes are important in which the adsorbent moves relatively to the walls of the containment vessel. The simplest process involves mixing a batch of adsorbent with a batch of fluid (Crittenden, 1998).

Shakir, (2002) used two different dye removal methods: chemical coagulation and adsorption through activated carbon. Adsorption through granular activated carbon was found to be very effective for the removal of the different dyes considered, where the percent dye removal was 96.7%, 98.7% and 98.4% for direct blue, sulphur black and vat yellow respectively.

Abood, (2004) Studied the furfural removal from wastewater by the adsorption process by activated carbon using continuous system (fixed-bed). Nineteen experiments were carried out to study the effect of various initial conditions (bed depth, flow rate, particle size of activated carbon, and influent concentration) on the performance of fixed bed.

Experimental Work

Material

Dye solution used in the present experiments was prepared by dissolving a weighed amount of the powder reactive blue dye (from textile factory in Hilla) in tap water.

Adsorbate is the reactive blue dye with chemical structure as shown in Fig (1), and molecular weight (637 g/mol).

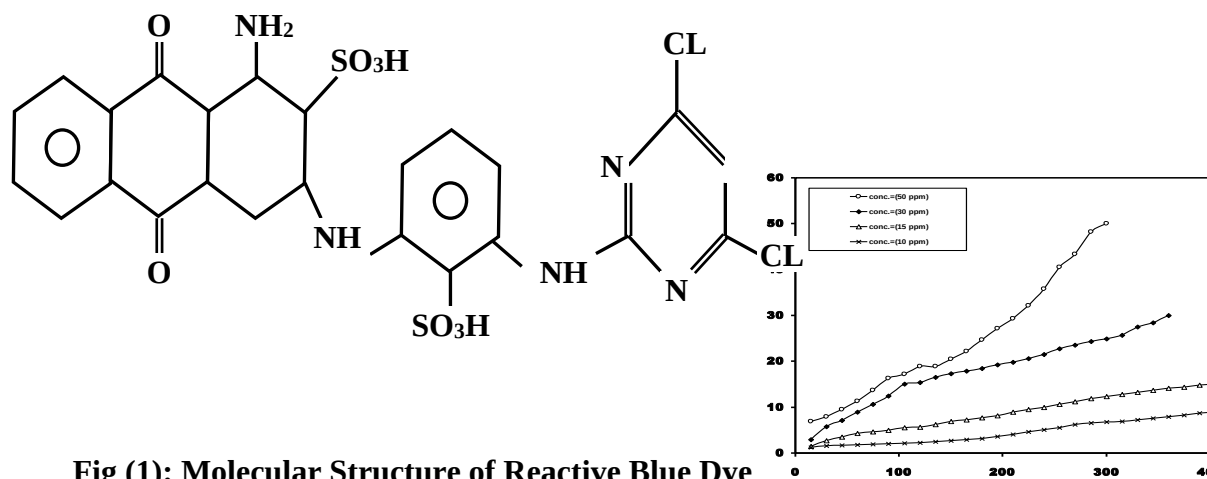


Fig (1): Molecular Structure of Reactive Blue Dye

Adsorbent is granular activated carbon (provided by Unicarbo Co. Italy) was used in the present work. It's physical properties are tabulated in table (1).

Table(1):Properties of activated carbon used in this research

ITEM OF ANALYSIS	SPECIFICATION	RESULTS	METHOD
Dimensions	-	12*40 mesh(0.4-1.6)mm	
Bulk density(kg/m ³)	460-520	460-480	ASTM D 2854-96
Void fraction	-	0.45	
Surface area(m ² /gm)	1000(min)	1100-1130	ASTM D 4607-96
Hardness (%)	97(min)	98(min)	ASTM D 3802-94
Ash(%)	5(max)	5(max)	ASTM D 4607-94
Micropore	-	High	

Activated carbon was washed with distilled water before being used to remove fines and dried at (110 C°) for (3600 s).

Equilibrium isotherm experiment

Granular activated carbon weights (2, 1.5, 1.0, 0.5, 0.25, and 0.1) g are placed in individual six flasks of (250 ml) volume. The same volume of wastewater (100 ml) with dye concentration (30 ppm) is added to each flask then shaken for about 8 h. The solution was filtered by filter paper and 3 ml of filtrate was analyzed using spectrophotometer type (CECIL CE 1000 SERIES) at λ (579 nm). Table (2).

Table (2): Experimental and theoretical equilibrium isotherm data

Equilibrium Concentration (ppm)	Experimental isotherm data $q_e(\text{kg/kg}) \cdot 10^{-4}$	Langmuir isotherm data $q_e(\text{kg/kg}) \cdot 10^{-4}$	Freundlich isotherm data $q_e(\text{kg/kg}) \cdot 10^{-4}$
20	100	101	107
10	80	75	68
5	50	50	44
3	27	34	32
1.3	19	17	19
1	15	13	16

Continuous adsorption experiments

The experimental work was done using the laboratory apparatus shown in Fig (2).

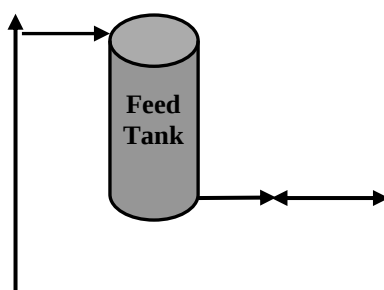


Fig (2): A schematic representation of experimental equipment

Table (3) shows the experimental conditions for all experiments containing the flow rate Q , initial dye concentration C_o , bed depth of carbon Z , and particle size of carbon $P.s.$

Table (3): Column system data

Data of experimental				
Exp. No.	$Q \cdot 10^{-5}$ (m ³ /min)	C_o (ppm)	$B.D \cdot 10^{-2}$ (m)	$P.S. \cdot 10^{-3}$ (m)
1	60	30	10	1.4-0.6
2	33.33	30	10	1.4-0.6
3	20	30	10	1.4-0.6
4	8.33	30	10	1.4-0.6
5	20	50	20	1.4-0.6
6	20	30	20	1.4-0.6
7	20	15	20	1.4-0.6
8	20	10	20	1.4-0.6
9	20	30	40	1.4-0.6
10	20	30	30	1.4-0.6
11	20	30	20	1.4-0.6
12	20	30	10	1.4-0.6
13	20	30	20	1.4-0.6
14	20	30	20	1.4
15	20	30	20	1.18
16	20	30	20	0.6

A vertical Pyrex column was used as fixed bed adsorber with inner diameter (5cm) and (80cm) height. This column was packed with different heights of activated carbon. The wastewater was introduced at the top of column and the samples were taken at interval time of (15 min) from the bottom of the column.

Efficiency removal

The efficiency removal of blue dye from wastewater can be calculated by

$$E\% = \frac{\text{input} - \text{output}}{\text{input}} \dots\dots\dots(1)$$

In this work the efficiency removal calculated by consider the output concentration of dye =10% input concentration of dye.

Batch System

The batch system was utilized to estimate the average surface diffusivity (D_s). This was achieved by obtaining the initial concentration of the batch experiment identical to the influent concentration of the column experiment.

A Pyrex glass cylinder (1 litter) was used as a reactor container. The cylinder was fitted with a variable speed (0-1000 rpm) and magnetic stirrer (PROLABO)

An accurately weighed amount of activated carbon (10×10^{-3} kg) was placed into the cylinder. The cylinder contained (1×10^{-3} l.) of an aqueous solution of (30 ppm) of reactive blue dye concentration. The activated carbon was immediately mixed with the solution by magnetic stirrer at room temperature and speed (900 rpm). . Every (15) minutes samples (3 ml) were taken out periodically by means of pipette for analysis until equilibrium is reached. The samples were filtered before the analysis using filter paper.

The concentration of the solute in the samples was determined by device of spectrophotometer. The results were plotted as (W_o/W_∞) (the quantity of adsorbate removed from bulk solution over the total quantity of adsorbate at equilibrium) versus time.

Measurement of Surface Diffusivity

The surface diffusivity (D_s) was obtained by comparing experimental uptake data with theoretical uptake data. Experimental data were obtained using batch system.

For granular of uniform size and littler rounded shape can be approximated by sphere of radius (R).

$$\frac{W_o}{W_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\lambda(1+\lambda)}{9\lambda(1+\lambda) + \lambda^2 q_n^2} \exp[-q_n^2 TH] \dots\dots\dots(2)$$

$$\lambda = (3V_l / 4\pi R^3)$$

q_n : Constants q_1, q_2

Where:

W_o / W_∞ :Fractional uptake (amount of adsorbate at given time/ amount of adsorbent at equilibrium)

λ : Effective volume ratio.

TH: Through put value dimensionless.

V_p :Volume of adsorbent. (m^3)

K_e :Sorption equilibrium constant.

R: Particle radius. (m)

By selecting mathematical model, theoretical (W_o/W_∞) will be obtained for each value of through put ($TH>0$) and value of time is being obtained from plot of experimental (W_o/W_∞) vs. time according to the theoretical values of (W_o/W_∞) Diffusion coefficient (D_s) will be obtained by relation of:

$$D_s = (TH R^2/t)$$

For each value of (TH) and time (t) when particle size (R) is known and average value of (D_s) will be estimated.

Results and Discussions

Equilibrium Isotherm Curve

Plot of q_e (Adsorbed amount per amount of carbon) vs. C_e (concentration at equilibrium for each sample of batch experiment) gives experimental isotherm curve, Fig (3)

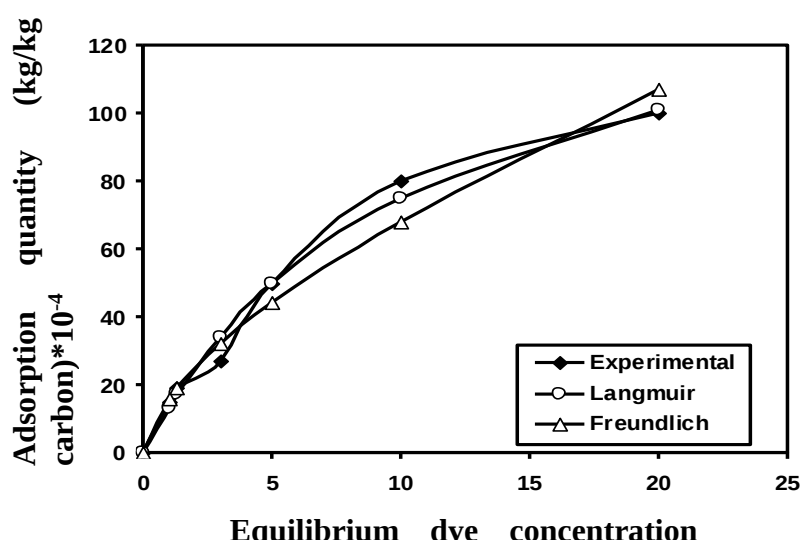


Fig (3): Experimental and theoretical data were obtained from the Langmuir and Freundlich equations for the adsorption quantity

where.

$$q_e = \frac{C_o - C_e}{m} \cdot V \quad \dots\dots(3)$$

q_e : Adsorbed amount per amount of carbon. (kg/kg)

C_o : Initial concentration of adsorbate. (kg/m^3)

C_e : Concentration of adsorbate at given time. (kg/m^3)

M: Mass of carbon. (kg)

V: Volume of the sample in the batch process. (ml)

Langmuir equation (Weber, 1972, Abdul-Hammed, 1996)

$$q_e = \frac{x}{m} = \frac{\bar{Q}bC_e}{1+bC_e} \quad \dots\dots\dots(4)$$

X: Amount of adsorbed material. (kg)
 $\bar{Q}$: Langmuir equation parameter. (kg/kg)
 b: Langmuir equation parameter. (m³/kg)

And the linear equation is:

$$\frac{C_e}{q_e} = \frac{1}{\bar{Q}b} + \frac{C_e}{\bar{Q}} \quad \dots\dots\dots(5)$$

Plot of (C_e/q_e) vs. C_e Fig (3) is to determine Langmuir constants ($\bar{Q}, b$), table (4) in order to estimate the theoretical (q_e) of Langmuir equation

Freundlich equation (Casey, 1992, Martin, 1979)

$$q_e = kC_e^{1/n} \quad \dots\dots\dots(6)$$

K: Freundlich equation parameter. (kg/kg)
 1/n: Freundlich equation parameter. (kg/m³)

And the linear equation is:

$$\text{Log}q_e = \text{Log}k + 1/n \text{Log}C_e \quad \dots\dots\dots(7)$$

Plot of ($\text{Log}q_e$) vs. ($\text{Log}C_e$) Fig(3) is to determine Freundlich constants (K, n), table (4) in order to estimate the theoretical (q_e) of Freundlich equation.

Table (4) Langmuir and Freundlich equation constants.

Equations	$\bar{Q}$ (kg/kg)	b (m ³ /kg)	K (kg/kg)	1/n (m ³ /kg)	St. Err.	Corr. Coeff.(R)
Langmuir	0.015	96			4.47	0.99
Freundlich			7.58	0.64	7.84	0.97

Effect of flow rate

The break through curves at different flow rate Fig (4) showed.

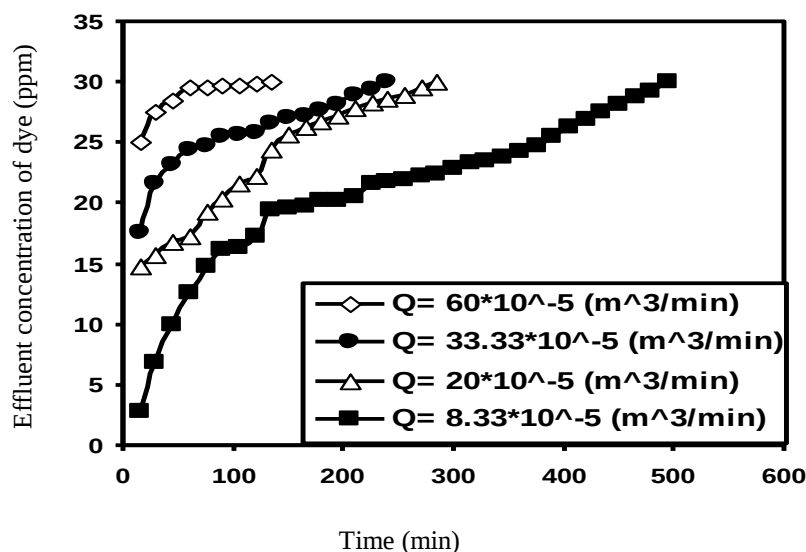


Fig (4): Break through curves of isotherm adsorption for different wastewater flow rate

when flow rate increases the break point time of the curve decreases and adsorption capacity decreases too Fig (5).

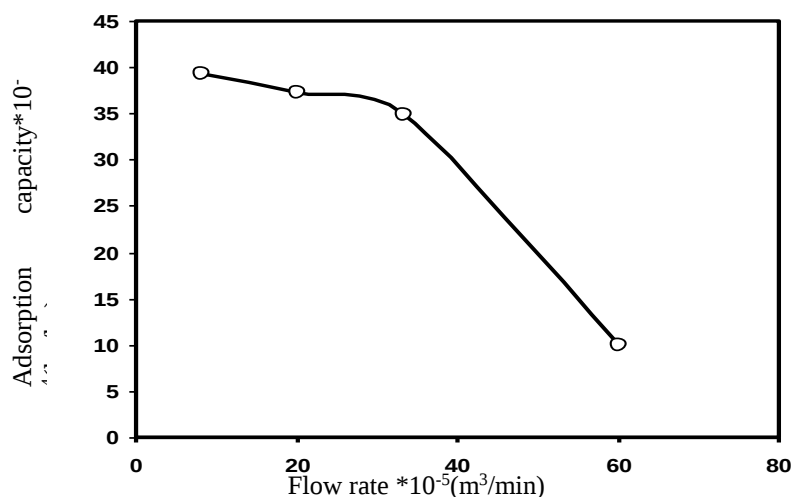


Fig (5): Effect of the wastewater flow rate on the adsorption capacity of activated carbon

This is due to increase the linear velocity and also decreases the contact time

Effect of initial influent concentration

Fig (6) showed low difference in breakpoint time at increasing of dye concentration.

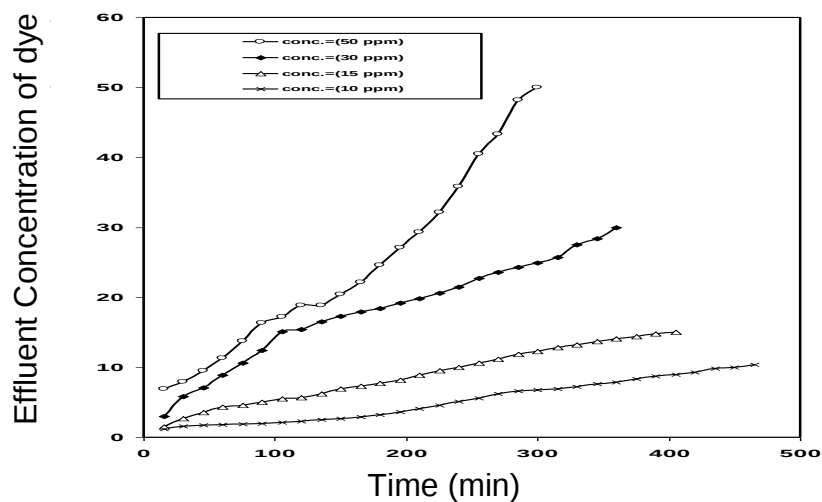
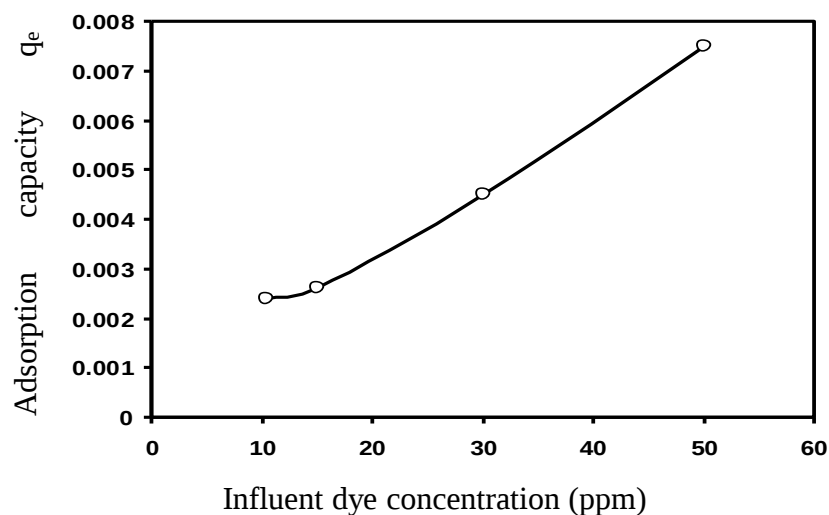


Fig (6): Break through curves of isotherm adsorption for different influent concentration of dye

But there is increase in the adsorption capacity Fig (7), this phenomena is due to the increasing the influent dye concentration which act as a driving force will increase the concentration difference between the bulk solution and solid phase.



Effect of bed depth

Fig (8) showed that the increasing the breakpoint time when carbon bed increases and adsorption capacity increases too Fig (9).

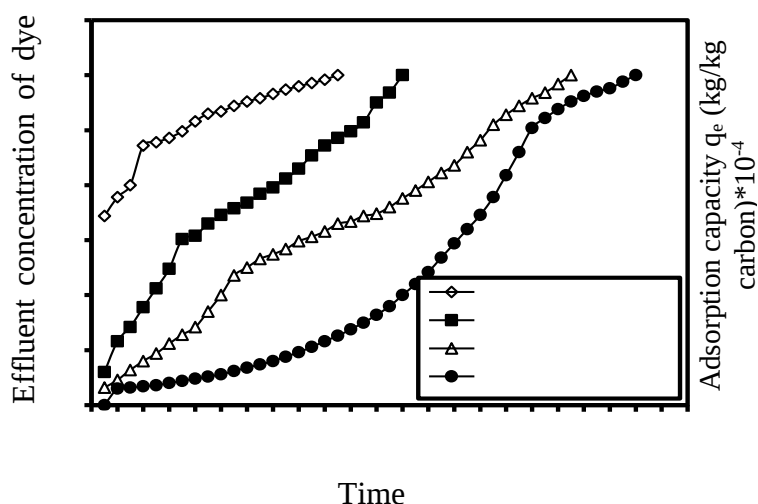


Fig (8) Break through curves of isotherm adsorption for different bed depth of activated carbon

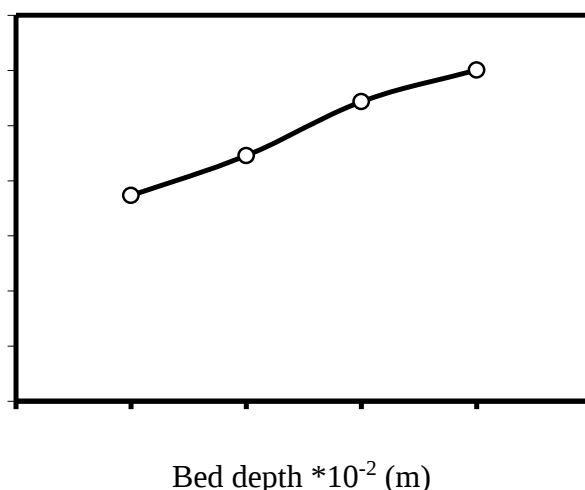


Fig (9) Effect of different bed depth of activated carbon on the adsorption capacity

This is due to provide extra surface area when carbon bed increases as well as the service life of bed increases.

Effect of particle size

The required time for reaching the breakpoint increased when particle size decreased Fig (10), and adsorption capacity increased too, Fig (11).

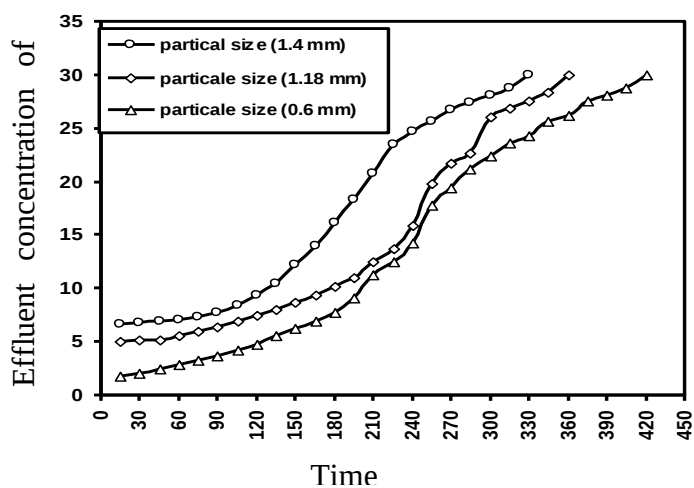


Fig (10) Break through curves of isotherm adsorption for different particle size of activated carbon

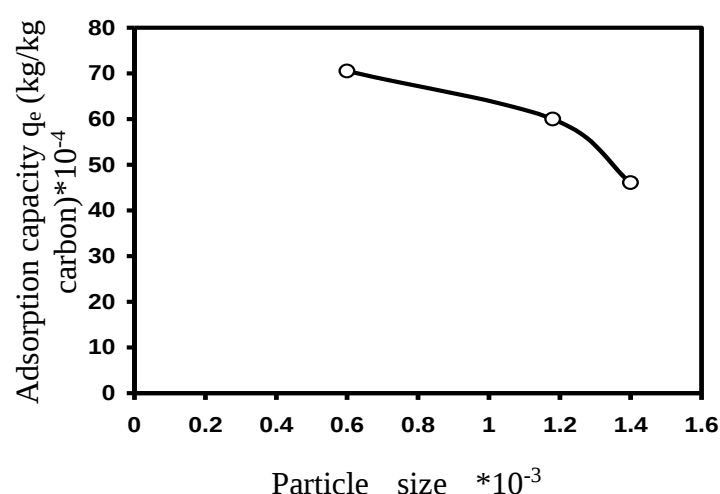


Fig (11) Effect of particle size of activated carbon on the adsorption capacity

This can be explained due to the opening a new pores when crushing the carbon to small particle size for process of the adsorption.

Measurement of surface diffusivity (D_s)

The results of (w_o/w_∞) from experimental batch process were against time. Fig (12).

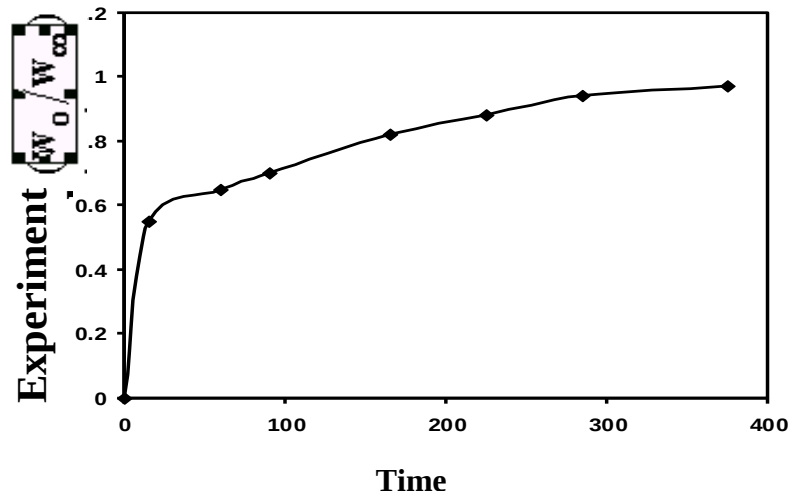


Fig (12) Experimental (w_o/w_∞) for batch Isotherm system at ($C_o=30$ ppm) and speed (900 rpm)

The theoretical values of (w_o/w_∞) were obtained from equation (2) for granular shape of activated carbon:

Where values of (q_n) were obtained from table (1). (Ludersen, 1983)

For $\lambda > 10$ $q_n \implies q_1=3.142$ $q_2=6.287$

Fig (13) shows the plotting of the theoretical value of (w_o/w_∞) against (TH), which were obtained from equation (2).

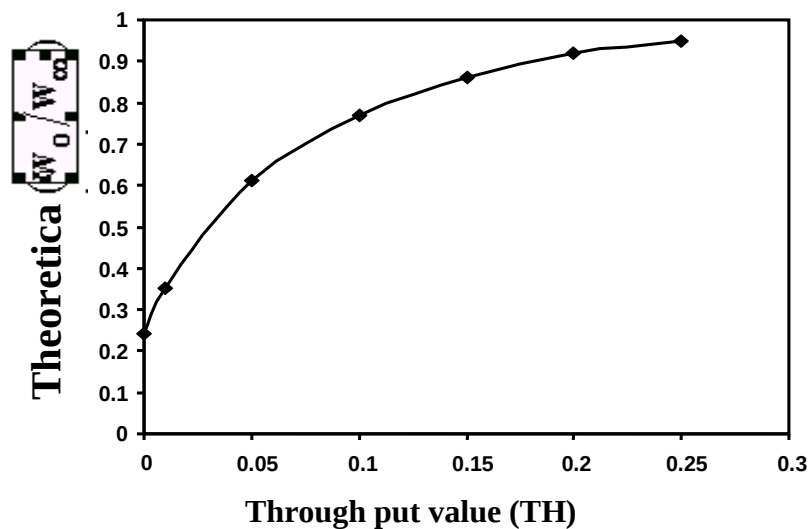


Fig (13): Plot of (w_o/w_∞) Vs. (TH) for determination of surface diffusivity ($TH= D_s t/R^2$) at ($\lambda > 10$)

The values of time (i.e. determination of surface diffusivity) were obtained from theoretical values of (w_o/w_∞) and Fig (12)

The values of (D_s) were obtained from the following relation ($D_s = TH R^2/t$), the values of (TH) from Fig (13) and known particle radius.

Multiple linear regression model

Applying multiple linear regression (using SPSS system) to the experimental data table (2) between the independent variables (Q, C_o , Z, and P.S) and the dependent variables (t, q) separately, the following correlations were obtained:

Cororr. Coef.

$$t = 540.0 - 5.3Q - 3.3 C_o + 8.8 Z - 112.5 P.S \quad 0.92 \quad (8)$$

$$q = 340.3 - Q + 1.3 C_o + 0.9 Z - 30.6 P.S \quad 0.95 \quad (9)$$

Where:

t: time (min) within the range (135-630).

q: the amount of adsorbate per unit weight of adsorbent (kg/kg of carbon) within the range $(9.96-74.82) \times 10^{-4}$.

Q: the flow rate (m^3/min) within the range $(8.33-60) \times 10^{-5}$.

C_o : the influent concentration (ppm) within the range (10-50).

Z: the bed depth of activated carbon (m) within the range $(10-40) \times 10^{-2}$.

P.s: the size of particle of activated carbon (m) within the range $(0.6-1.4) \times 10^{-3}$.

Verification for these equations can be made by plotting the experimental data versus modeling data as shown in Fig (14) and Fig (15); these figures showed that the experimental data are correlated well within the modeling data.

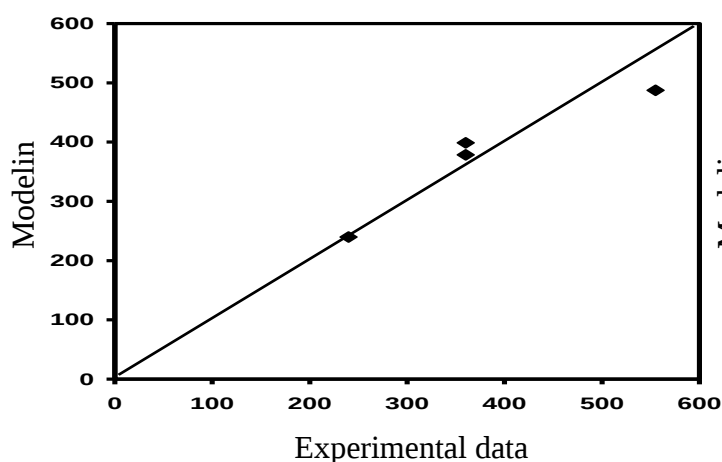


Fig (14): Verification for equation (8)

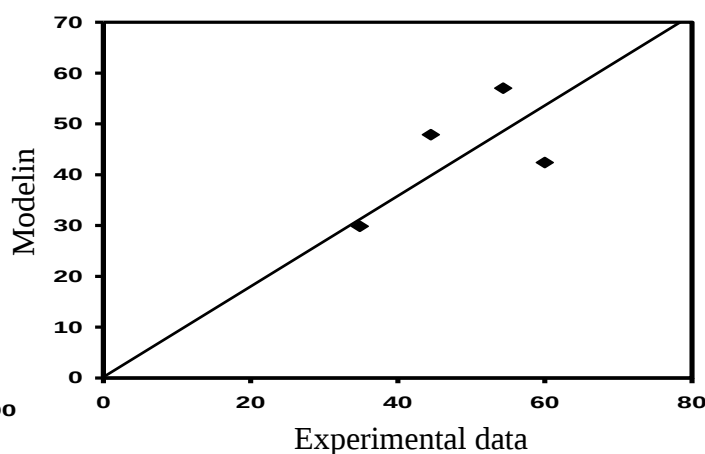


Fig (15): Verification for equation (9)

Conclusions

1. The equilibrium isotherm for the system of adsorbed blue dye on activated carbon was a favorable type, and was well represented by Langmuir and Freundlich equations.
2. The time required for reaching saturation of activated carbon increases with decreasing flow rate of wastewater, increasing bed depth, decreasing influent concentration and decreasing particle size.
3. The capacity of activated carbon increased with increasing bed depth and influent concentration and also increased with decreasing flow rate and particle size.

4. The following correlations were obtained by applying multiple regression and represent the best fitting for the experimental data.
 $t = 540.0 - 5.3Q - 3.3C_o + 8.8Z - 112.5 P.S$
 $q = 34.3 - 0.7Q + 1.3 C_o + 0.9Z - 30.6 P.S$
5. The adsorption process using activated carbon insures an excellent degree of reduction for color with removal efficiency 90%.

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Nomenclature

b:	Langmuir equation parameter.	(m ³ /kg)
C _e :	Concentration of adsorbate at given time.	(kg/m ³)
C _o :	Initial concentration of adsorbate.	(kg/m ³)
K:	Freundlich equation parameter.	(kg/kg)
K _e :	Sorption equilibrium constant.	
m:	Mass of carbon.	(kg)
1/n:	Freundlich equation parameter.	(kg/m ³)
P.s:	size of particle of activated carbon in	(m)
q:	is the amount of adsorbate per unit weight of adsorbent in (kg/kg of carbon)	
q _n :	Constants of theoretical model of batch process	
Q:	flow rate	(m ³ /min)
$\bar{Q}$:	Langmuir equation parameter.	(kg/kg)
R:	Particle radius.	(m)
t:	time	(min)
TH:	Through put value dimensionless.	
V:	Volume of the sample in the batch process.	(ml)
V _p :	Volume of adsorbent.	(m ³)
W _o / W _∞ :	Fractional up take (amount of adsorbate at given time/ amount of adsorbent at equilibrium)	
X:	Amount of adsorbed material.	(kg)
Z:	bed depth of activated carbon	(m)
λ :	Effective volume ratio.	