

# REMOVAL OF BLUE DYE FROM WASTEWATER BY ADSORPTION ONTO ACTIVATED CARBON

Prof. Dr. Abass H. Sulaymon  
Asst. Prof. Dr. Mohammad A. Moslem Al-Tufaily  
Afrah A. Hassan

## 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 منحنى 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 (P.S ، Z ، C<sub>o</sub> ، Q) والمتغيرات المعتمدة (كمية المادة الممتزة (q)، ووقت الامتزاز (t)) كل على حدة. ان عمل تحقيق لهذه العلاقات وإيجاد معامل الترابط (0.94 ، 0.92) للعلاقتين 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.

**Key words: Blue dye, Adsorption, Activated carbon, Adsorption capacity, Langmuir and Freundlich equations, Fixed bed adsorber.**

## **1. INTRODUCTION:**

Adsorption onto solid can be defined as the phenomena that taking up the molecules from the fluid phase onto the solid surface (Kirk and Othmer, 1947). 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 (Kirk and Othmer, 1947).

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.

## **2. Experimental Work**

### **2.1. 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).

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).

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

## **2.2. 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  $\lambda$  (579 nm). Table (A-1), Appendix A.

## **2.3. Continuous adsorption experiments:**

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

A vertical Pyrex column was used as fixed bed adsorber with inner diameter (5cm) and (80 cm) 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.

## **2.4. Removal of efficiency:**

The removal of efficiency 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 removal efficiency calculated by consider the output concentration of dye =10% input concentration of dye.

## **3. 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 liter) 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 ( $10 \times 10^{-3}$  kg) was placed into the cylinder. The cylinder contained ( $1 \times 10^{-3}$  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 ( $W_o/W_\infty$ ) (the quantity of adsorbate removed from bulk solution over the total quantity of adsorbate at equilibrium) versus time.

### **3.1. 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 as described by (Carman and Houl, 1954 and (Grank, 1957).

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

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

$$\lambda = (3 V_1 / 4\pi R^3)$$

$q_n$ : Constants  $q_1, q_2$

Where:

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

$\lambda$  : Effective volume ratio.

$q_n$  :Constants of theoretical model of batch process.

TH: Through put value dimensionless.

$V_p$  :Volume of adsorbent. (m<sup>3</sup>)

$K_e$  :Sorption equilibrium constant.

R: Particle radius. (m)

By selecting mathematical model, theoretical ( $W/W_0$ ) will be obtained for each value of through put (TH>0) and value of time is being obtained from plot of experimental ( $W/W_0$ ) vs. time according to the theoretical values of ( $W/W_0$ ). 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.

## 4. Results and Discussions

### 4.1. 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) 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<sup>3</sup>)

$C_e$ : Concentration of adsorbate at given time. (kg/m<sup>3</sup>)

M: Mass of carbon. (kg)

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

**4.2. Langmuir equation** (Weber, 1972, Abdul-Hammed, 1996)

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

- X: Amount of adsorbed material. (kg)
- $\bar{Q}$ : Langmuir equation parameter. (kg/kg)
- b: Langmuir equation parameter. (m<sup>3</sup>/kg)

And the linear equation is:

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

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.

**4.3. Freundlich equation** (Casey, 1992, Martin, 1979)

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

- K: Freundlich equation parameter. (kg/kg)
- 1/n: Freundlich equation parameter. (kg/m<sup>3</sup>)

And the linear equation is:

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

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.

#### **4.4. Effect of flow rate:**

The break through curves at different flow rate Fig (4) showed, when flow rate increases the break point time of the curve decreases and adsorption capacity decreases too Fig (5).

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

#### **4.5. Effect of initial influent concentration:**

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

#### **4.6. Effect of bed depth:**

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

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

#### **4.7. 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).

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

The experimental result were tabulated in table (A-1)- (A-5), Appendix A.



#### **4.8. Measurement of surface diffusivity ( $D_s$ ):**

The results of  $(\mathbf{w}_o/\mathbf{w}_\infty)$  from experimental batch process were against time. Fig (12).

The theoretical values of  $(\mathbf{w}_o/\mathbf{w}_\infty)$  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  $(\mathbf{w}_o/\mathbf{w}_\infty)$  against (TH), which were obtained from equation (2)

The values of time (i.e. determination of surface diffusivity) were obtained from theoretical values of  $(\mathbf{w}_o/\mathbf{w}_\infty)$  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.

The experimental result were tabulated in table (A-6), Appendix A.

#### **5. 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:

	<b><u>Cororr. Coef.</u></b>	
$t=540.0 -5.3Q -3.3 C_o +8.8 Z -112.5 P.S$	0.92	(8)
$q=340.3-Q +1.3 C_o +0.9 Z -30.6 P.S$	0.95	(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  $(9.96-74.82)*10^{-4}$ .

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

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

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

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.

### **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%.

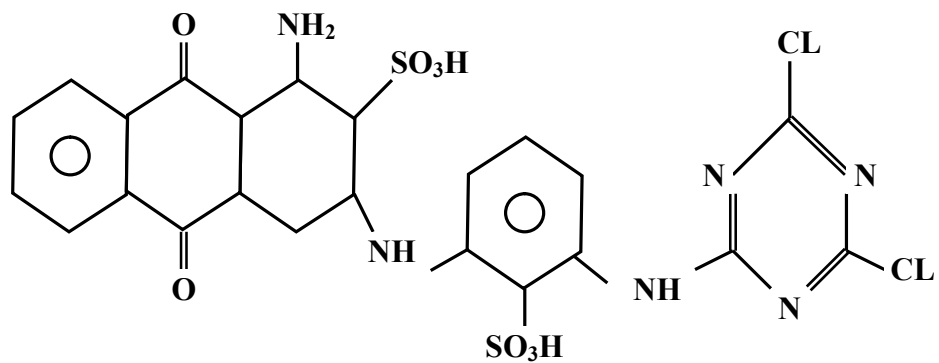
## References:

1. Abdul-Hammed, H. M., (1996) :("Reduction of organic content in wastewater by adsorption onto activated carbon". M.Sc. Thesis, College of Eng., Univ. of Baghdad, Iraq.
2. Abu Regebaa, Y. A. Z. M., (1992): "**Removal of pollutants from water by adsorption**". M.Sc. Thesis, College of Engineering, University of Baghdad, Iraq.
3. Abood, W. M., (2004): "**Designing of pilot plant for treatment of wastewater contaminated by the furfural**". M. Sc. Thesis, College of engineering, University of Baghdad, Iraq.
4. Carman, P. C. and Houl, R. A., (1954): "**Measurement of diffusion coefficient**". J. Proc. Roy. Soc., 222A, PP.109.
5. Casey T. J., (1992): "**Unit Treatment Processes in Water and Wastewater Engineering**". Wiley Series, New York, "The International Conference on Water and the Environment".
6. Crittenden, B. and Thomas, W. J., (1998): "**Adsorption technology and design**". Butter Worth and Heinemann, Woburn, UK.
7. Erskine, D. B. and Schuliger, W. G., (1971): "**Activated carbon processes for liquid**". Chem. Eng. Prog., Vol.67, No.11, PP.41.
8. Grank, J., (1957): "**The mathematical of diffusion**". PP. 84, Amen House, London.
9. Hassan, A. A., (2005): "**Removal of blue dye from wastewater by adsorption onto activated carbon**". M. Sc. Thesis, College of engineering, University of Babylon, Iraq.
10. Jason, P. P., (1999): "**Activated carbon and some applications for the remediation of soil and ground water pollution**". Naraine Persand, Virginia Tech.

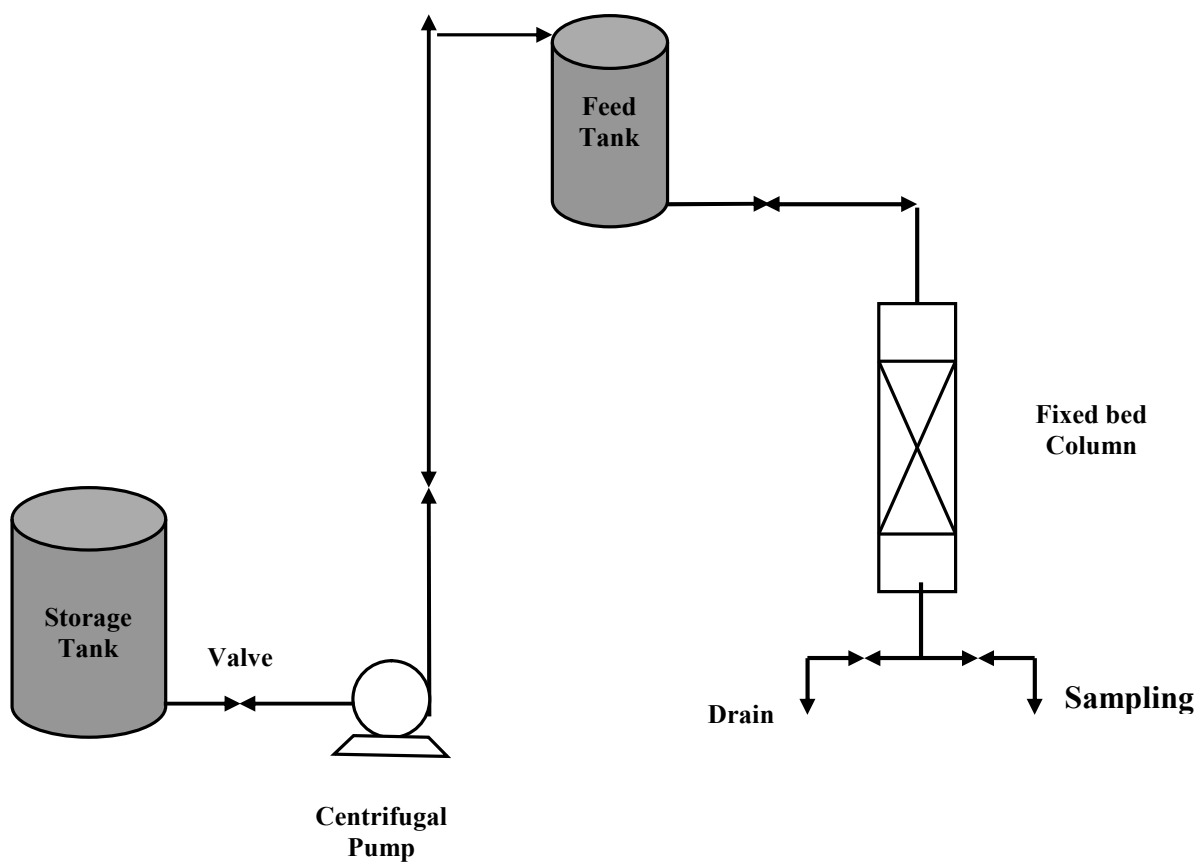
11. Kirk R. E. and Othmer D. F., (1947): “**Encyclopedia of Chemical Technology**”. Mack printing Co., Easton, U.S.A., Vol.1, PP.206-232.
12. Ludersen, A. L., (1983): “**Mass transfer in engineering practice**”. John Wiley and Sons, New York, ch. 7.
13. Martine, R. J. and Al-Bahrani, K. S., (1978) :(**Adsorption studies using gas-liquid chromatography-III. Experimental of factors influencing adsorption**”. J. Water Research, Vol.12, PP.879-888.
14. Martine, R. J. and Al-Bahrani, K. S” :(1979) “**Adsorption studies using gas-liquid chromatography-IV. Adsorption from bisolute-systems**”. J. Water Research, Vol.13, PP.1301-1304.
15. Poots V. J. P., Mckay, G. and Healy J. J., (1976” :(**The removal of acid dye from effluent using natural adsorbents**”. J. Water Research, Vol.10, PP.1061.
16. Shakir, E. K., (2002): “ **Study of industrial wastewater treatment and recycling process for cotton-textile industry**”. D. Ph. Thesis, College of Engineering, University of Baghdad, Iraq.
17. Weber W. J., (1972): “**physiochemical Processes for Water Quality Control**”. Wiley-Inter Science, New York.

## Nomenclature:

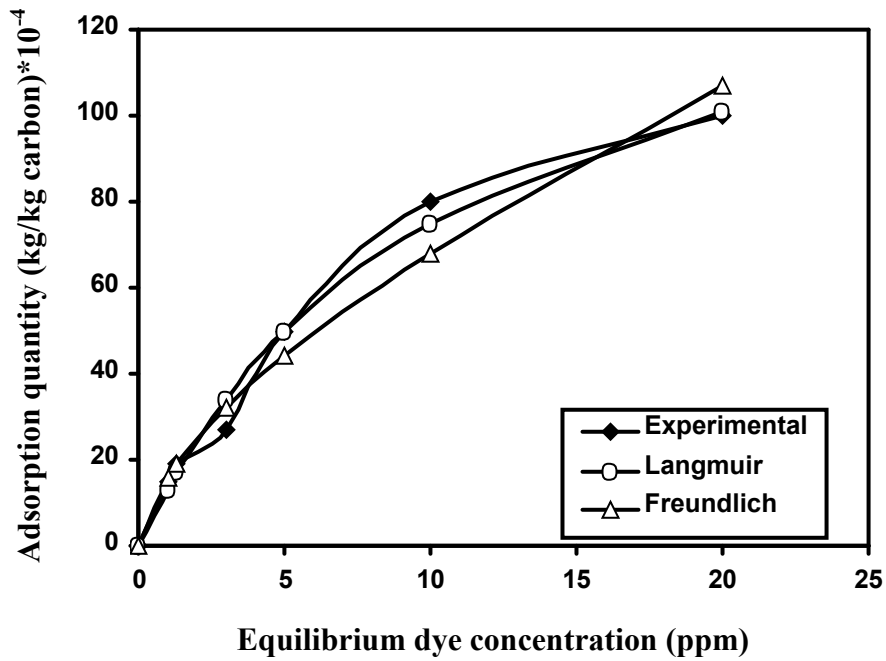
b:	Langmuir equation parameter.	(m <sup>3</sup> /kg)
C <sub>e</sub> :	Concentration of adsorbate at given time.	(kg/m <sup>3</sup> )
C <sub>0</sub> :	Initial concentration of adsorbate.	(kg/m <sup>3</sup> )
K:	Freundlich equation parameter.	(kg/kg)
K <sub>e</sub> :	Sorption equilibrium constant.	
m:	Mass of carbon.	(kg)
1/n:	Freundlich equation parameter.	(kg/m <sup>3</sup> )
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 <sub>n</sub> :	Constants of theoretical model of batch process	
$\overline{Q}$ :	flow rate	(m <sup>3</sup> /min)
$\overline{Q}$ :	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 <sub>p</sub> :	Volume of adsorbent.	(m <sup>3</sup> )
W <sub>0</sub> / W <sub>∞</sub> :	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.	



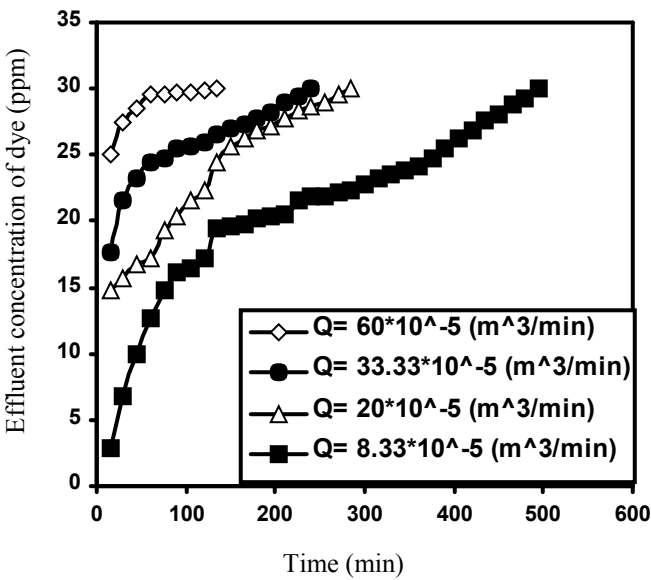
**Fig (1): Molecular Structure of Reactive Blue Dye**



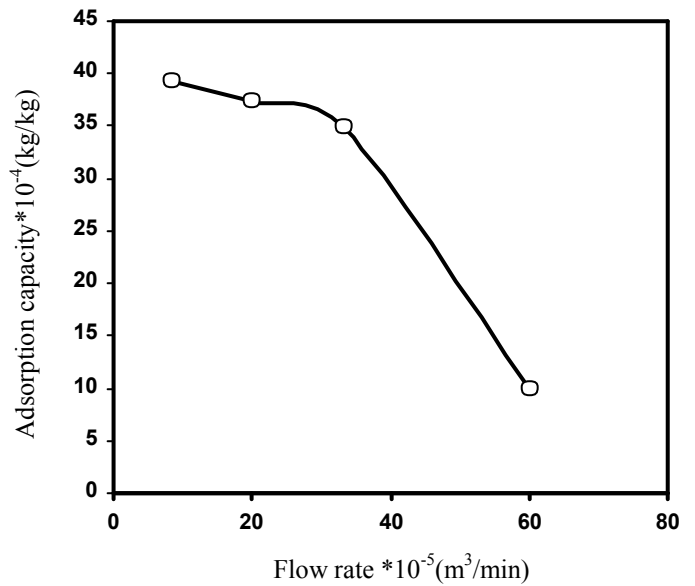
**Fig (2): A schematic representation of experimental equipment**



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



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



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

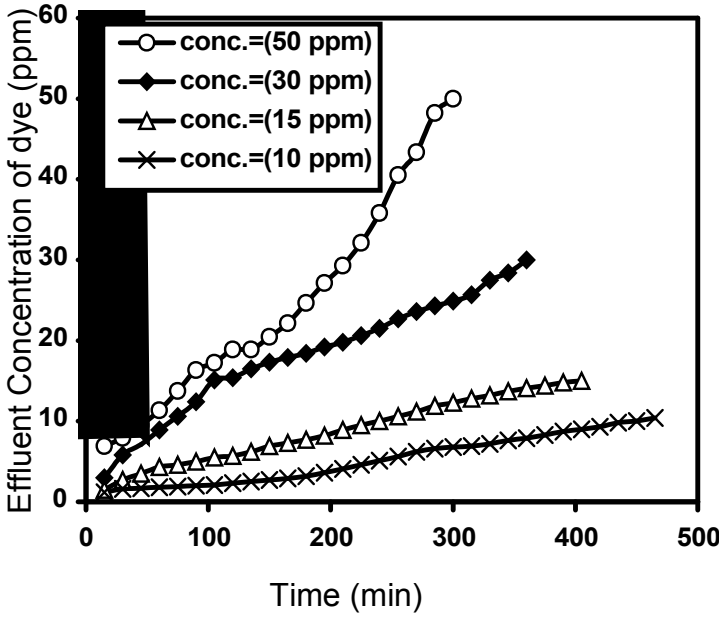


Fig (6): Break through curves of isotherm adsorption for different influent concentration of dye

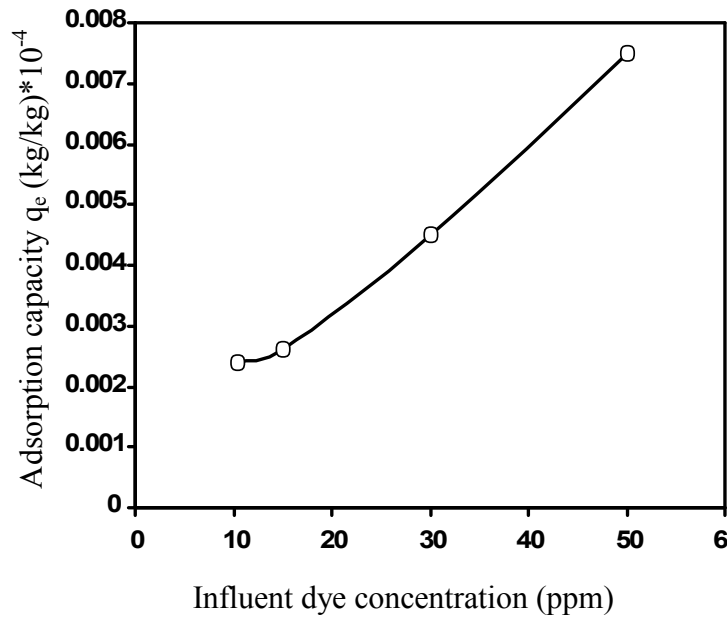


Fig (7): Effect of different influent concentration on the adsorption capacity of activated carbon

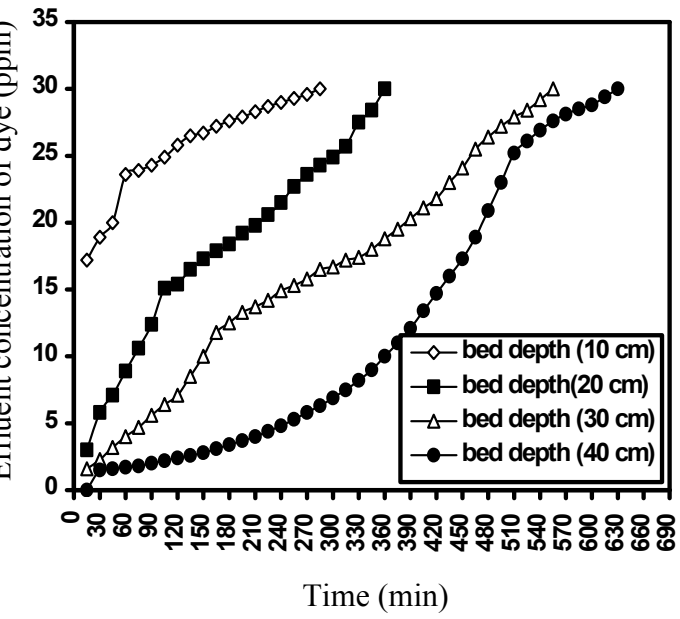


Fig (8): Break through curves of isotherm adsorption for different bed depth of activated carbon

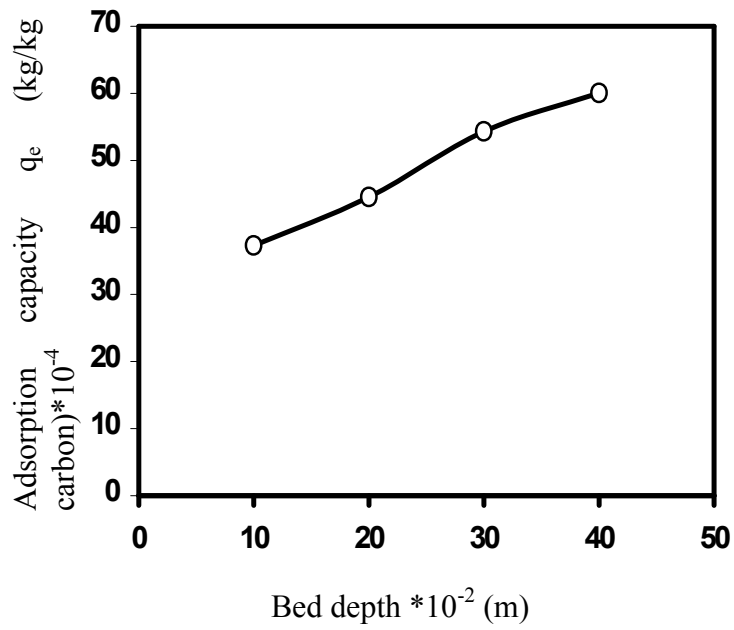


Fig (9): Effect of different bed depth of activated carbon on the adsorption capacity



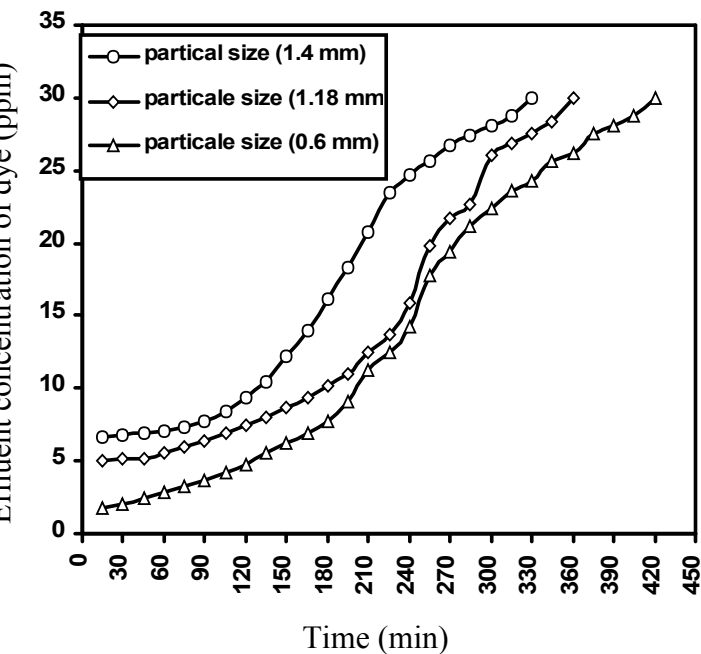


Fig (10) Break through curves of isotherm adsorption for different particle size of activated carbon

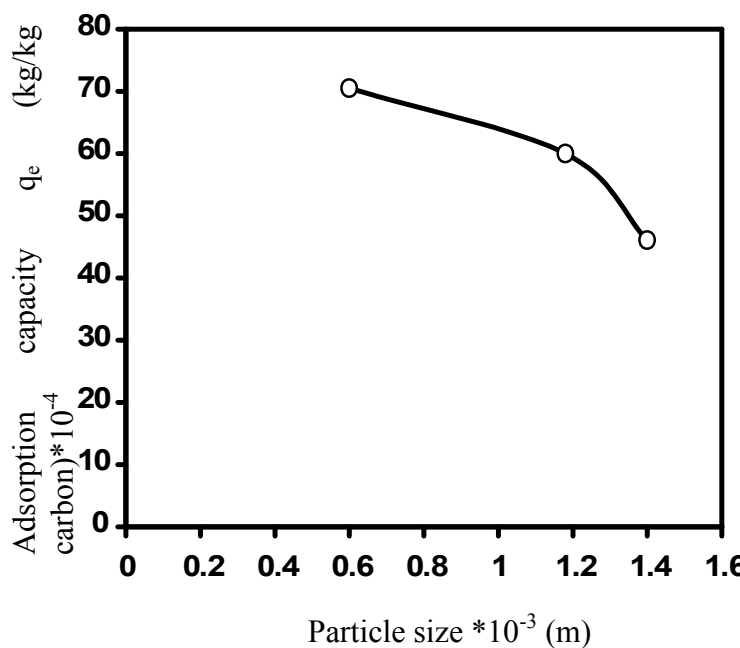


Fig (11) Effect of different particle size of activated carbon on the adsorption capacity

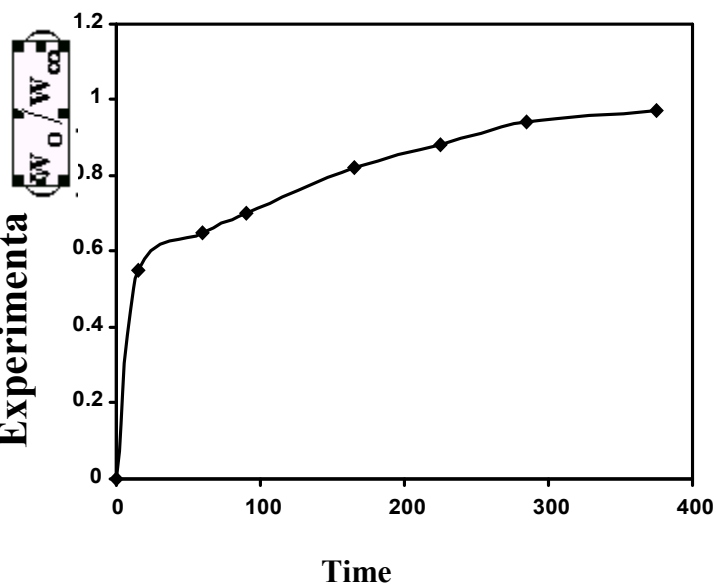


Fig (12) Experimental  $(W_0/W_\infty)$  for batch isotherm system at  $(C_0 = 30 \text{ ppm})$  and speed (900 rpm)

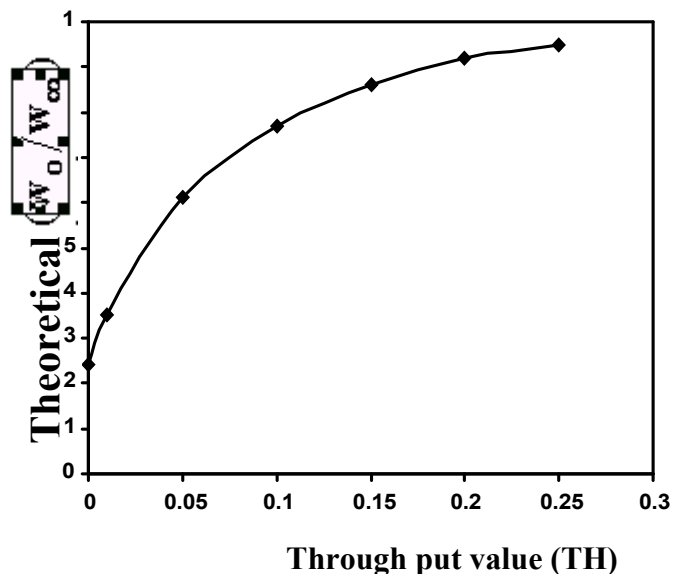
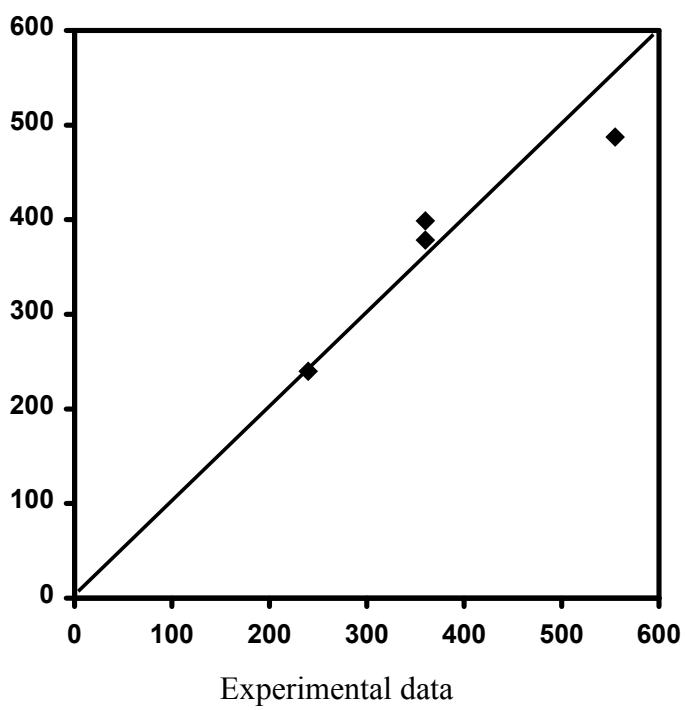
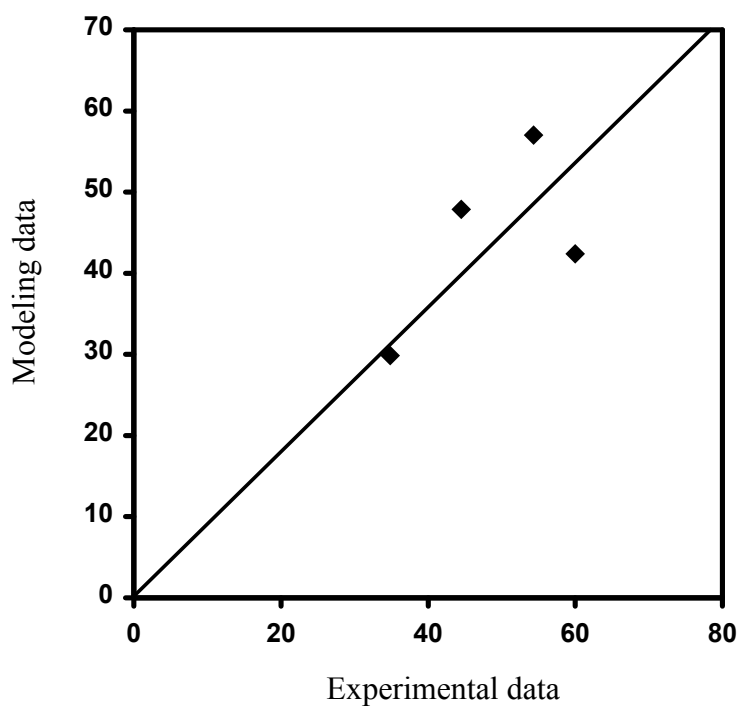


Fig (13): Plot of  $(W_0/W_\infty)$  Vs. (TH) for determination of surface diffusivity  $(TH = D_s t/R^2)$  at  $(\lambda > 10)$



**Fig (14): Verification for equation (8)**



**Fig (15): Verification for equation (9)**

**Table (1): Properties of Activated Carbon used in this Research**

ITEM OF ANALYSIS	SPECIFICATION	RESULTS	METHOD
Dimensions (granular)	-	12*40 mesh(0.4-1.6)mm	
Bulk density(kg/m <sup>3</sup> )	460-520	460-480	ASTM D 2854-96
Void fraction	-	0.45	
Surface area (m <sup>2</sup> /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	

**Table (2): Column system data**

Data of experimental				
Exp. No.	$Q \cdot 10^{-5}$ (m <sup>3</sup> /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

**Table (3): Column system data**

Data of results		
$M \cdot 10^{-3}$ (kg)	$q \cdot 10^{-4}$ (kg/kg)	Saturation time (min)
95	9.96	135
95	34.86	240
95	37.29	285
95	39.32	495
190	74.82	300
190	44.52	360
190	25.77	405
190	24.96	465
380	60.05	630
285	54.33	555
190	44.52	360
95	37.29	285
190	43.26	450
190	46.07	330
190	59.99	360
190	70.52	420

**Table (3) Langmuir and Freundlich equation constants.**

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