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Research Article

THE USE OF NON-LINEAR OPTIMIZATION BASED ON STATISTICAL ERROR CALCULATION OF ADSORPTION PROCESS OF ACID DYE ONTO GRANULAR ACTIVATED CARBON

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ABSTRACT

This paper deals with the removal of indigo carmine from aqueous solution using granular activated carbon in the batch method experiments. Correlated data were evaluated by using the non-linear regression of Langmuir, Freundlich, Liu, Khan and Redlich Peterson isotherm models. We found that the adsorption process can be favorably agreed by the Liu isotherm compared with the others models. Furthermore, the kinetic data were modeled using the Pseudo-first order, Pseudo-second order, Elovich equation, and Avrami fractionary kinetic equation. The results obtained show that the adsorption of indigo carmine on granular activated carbon follows the Avrami fractionary kinetic adsorption model. Thermodynamic parameters such as enthalpy ΔH°, entropy ΔS° and free enthalpy ΔG° were also evaluated to predict the nature of adsorption. The results indicate that the adsorption process is spontaneous and endothermic with increased disorder at the solid-solution interface during the adsorption.

Keywords: Activated carbon; indigo carmine; adsorption; isotherm; kinetic; non-linear regression.

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1. INTRODUCTION

The existence of dyes have been recognized as one of the most important noxious contaminants that the world is facing in today's age, when discharging in water even at very low concentrations, it has been difficult to degrade due to their complex aromatic structure and are generally resistant to light, temperature and to oxidizers agents[1-3]. In hence, these toxic effluents in general are suspected to be danger, carcinogens causing a pollution in oceans, underground water and damage to human health or other living species [4-6]. Consequently, it is necessary to treat them before discharging to aquatic system. In fact, the various synthetic dyes are widely employed in paper, cosmetics, printing, textile and food [7,8], for instance, Indigo carmine, a vat dye, is mainly used for dyeing polyester fibers, denim, sweets and cosmetics. It may cause allergic reactions, irritations of the skin, gastrointestinal symptoms, vomiting and respiratory problems [9-11]. There are a number of methods has been used for color removal including adsorption with activated carbon which is employed as one of the most successful and promising means to treat wastewater due to their simplicity in practical and low cost[12-14] . In this work, we show an experimental study to examine the adsorption capacity of indigo carmine onto granular activated carbon. The adsorbent dosage, pH and temperature, were estimated on the removal of indigo carmine followed by the isotherm and kinetic data to describe the adsorption process.

NOMENCLATURE

IC : indigo carmine

CAG: granular activated carbon

q_t : amount of IC adsorbed at time t ($mg.g^{-1}$)

q_e : amount of adsorbed IC per unit activated carbon mass at equilibrium ($mg.g^{-1}$)

q_m : maximum adsorption capacity ($mg.g^{-1}$)

C_0 : initial concentration of IC ($mg.L^{-1}$)

C_t : residual concentration of IC at time t ($mg.L^{-1}$)

C_e : residual concentration of IC at equilibrium ($mg.L^{-1}$)

V : solution volume (L)

m : activated carbon mass (g)

t : contact time (min)

T : absolute temperature (K)

v : agitation speed (rotation per minute or rpm)
K_L : equilibrium constant of Langmuir isotherm ($L.mg^{-1}$)
K_F : Freundlich isotherm constant ($mg^{(1-n)}.L^n.g^{-1}$)
n_F : adsorption intensity (Without units)
K_g : equilibrium constant of Liu isotherm ($L.mg^{-1}$)
b_K : Khan isotherm constant ($L.mg^{-1}$)
a_K : Khan isotherm model exponent.
K_R : Redlich-Peterson constants ($L.g^{-1}$)
a_k :Redlich-Peterson constants ($L.mg^{-1}$)
g :an exponent which lies between 0 and 1
n_L :dimensionless exponent of the Liu equation
N : number of experiments performed
P : number of parameters of the fitted model
R : universal gas constant (8.314 $J.mol^{-1}.K^{-1}$)
k_1 : pseudo-first-order adsorption rate constant (min^{-1})
k_2 : pseudo-second-order adsorption rate constant ($g.mg^{-1}.min^{-1}$)
h_0 : initial sorption rate for pseudo-second-order adsorption ($mg.g^{-1}.min^{-1}$)
α : initial adsorption rate ($mg.g^{-1}.min^{-1}$)
β : adsorption constant related to the surface coverage ($g.mg^{-1}$)
k_{AV} :Avrami kinetic constant (min^{-1})
n_{AV} :fractional adsorption order
ΔH^0 : adsorption enthalpy ($kJ.mol^{-1}$)
ΔG^0 :free energy of adsorption ($kJ.mol^{-1}$)
ΔS^0 :adsorption entropy ($J.K^{-1}.mol^{-1}$)

2. EXPERIMENTAL

2.1 Materials

The dye used in this study is indigo carmine (IC or E132) produced by Merck. IC is an anionic (acid) dye in the class of indigoids of chemical formula $C_{16}H_8N_2Na_2O_8S_2$ and molar mass 466.353g/mol. The structural formula of the molecule is shown in Fig.1

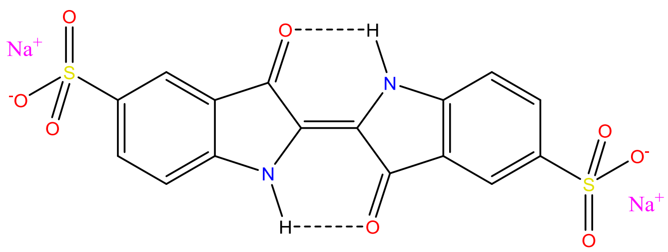

Fig.1. Chemical structure of indigo carmine

The commercial granular activated carbon (GAC) of vegetal origin used on this work was purchased from Prolabo. The GAC has a medium particle size <3mm. The GAC had 36 A° average pore (pore diameter greater than 20 A°), therefore, it is a mesoporous texture with specific surface area equal to ~ 988 m^2 / g.

2.2 Procedure

For retention studies, the experiments were conducted by adding a known amount of CAG into 25 mL of 35 mg/L dye solution at 20°C. The solution of dye was stirred at 200rpm in different time intervals to determine the amount of dye adsorbed. Then, the sample was centrifuged at 3600tr/min to remove the adsorbent .The determination of the concentration of dye was measured on a spectrophotometer (UV-Vis spectronic 70) at λ_{max}(nm) =609nm The dye amount adsorbed on activated carbon (adsorption capacity – q) was calculated using (Eq. (1)) [15]:

$$q_t=\frac{(C_0-C_t)}{m}\times V \quad (1)$$

The amount of IC adsorbed onto CAG at equilibrium, qe (mg/g), was calculated by the following expression:

$$q_e=\frac{(C_0-C_e)}{m}\times V \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 SEM analysis

The morphology of CAG before and after adsorption was characterized by SEM (Joel-JSM-6360LV). It is clear from the figure2 that the surface of CAG before adsorption (fig.2-a) defines a pore morphology and heterogeneous surface thus make a possibility of dye to be trapped. Respectively, it can also seen that the surface of CAG before and after adsorption (fig.2-b) is different which may due to the penetration of the molecules of indigo carmine on the surface of granular activated carbon resulting an decrease on the pore distribution.

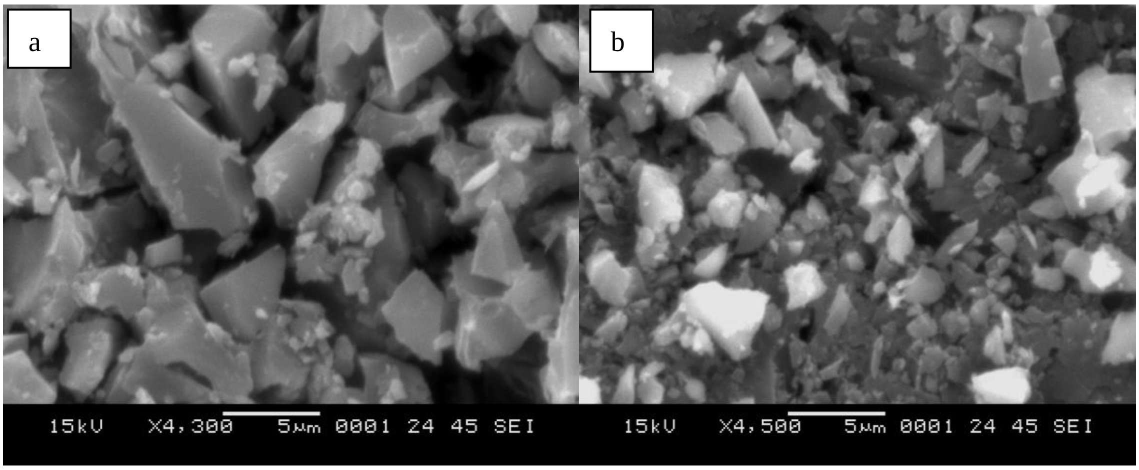

Fig.2. SEM micrographs of CAG surface (a) before adsorption and (b) after adsorption

3.2 Effect of initial adsorbent dosage

The influence of the mass of the activated carbon was studied in the range 1000-3000 mg.The obtained results are shown in fig3. From these results, it seems clear, with an increase in the adsorbent amount that the uptake capacity of activated carbon for indigo carmine was found to decrease. Adsorption capacity decreased from 0.85 mg/g at 1000 mg to 0.29 mg/g at 3000 mg for a contact time of 210 min. The decrease of adsorption capacity with increasing the activated carbon mass is attributed to the decrease of the adsorbent total surface area and the increase in diffusion path length due to the aggregation of adsorbent particles.This aggregation would lead to a reduction in the total surface area of the adsorbent [16,17].

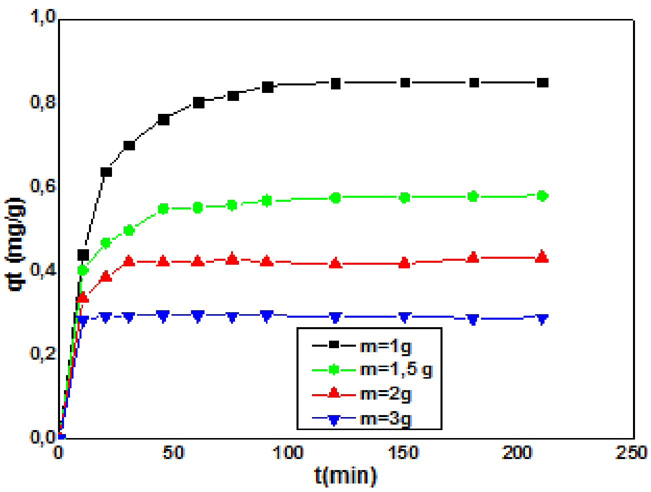

Fig.3. The effect of adsorbent dosage on the removal of indigo carmine by CAG for different time intervals (C_0=35mg/l, T=20°C, V=200 rpm)

3.3 Effect of pH

The pH was a significant factor in adsorption phenomena. Because it affects the shape, structure of dye and chemical properties of adsorbent .The effect of initial pH on dye removal of indigo carmine was investigated in the range 2 to 10. The figure 4 shows that the equilibrium time remains independent of the pH and that the highest adsorption capacity was achieved at the lowest pH. This can be explained by the fact that, in the acid medium, the positive charge dominates the surface of the adsorbent. Thus, a substantially high electrostatic attraction exists between the positive charges of the surface of the adsorbent and the anionic dye. At basic pH, despite of the presence of OH^-, we have found that the adsorption capacity is greater than that at neutral pH, so that we can say that there is always an attraction between the dye and the adsorbent and there is little competition between the OH^- and the anionic dye [18-20].

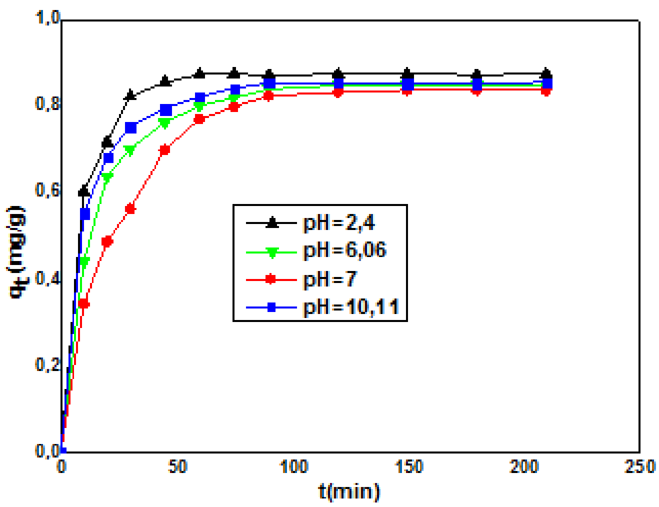

Fig.4. The effect of pH on the removal of indigo carmine by CAG for different time intervals (C_0=35mg/l, m=1g, T=20°C, V=200 rpm)

3.4 Effect of temperature

From the fig 5, it is noticed that the temperature is a remarkable parameter on the adsorption rate. The effect of temperature on the removal of indigo carmine dye by CAG was evaluated within the temperature range 288K to 313K.The results showed when the temperature increasing the amount of adsorbed dye increase, with 0,771 to 0,874 at the end of 75 min of operation. Therefore it’s confirmed that the difference in temperature had significantly effect on the kinetic adsorption as well as the rate of penetration of the dye molecule into the internal pores of the adsorbent particle, owing the reduction of the viscosity of the solution which means also that the adsorption of indigo carmine on granular activated carbon could be endothermic in nature (ΔH>0) [21,22].

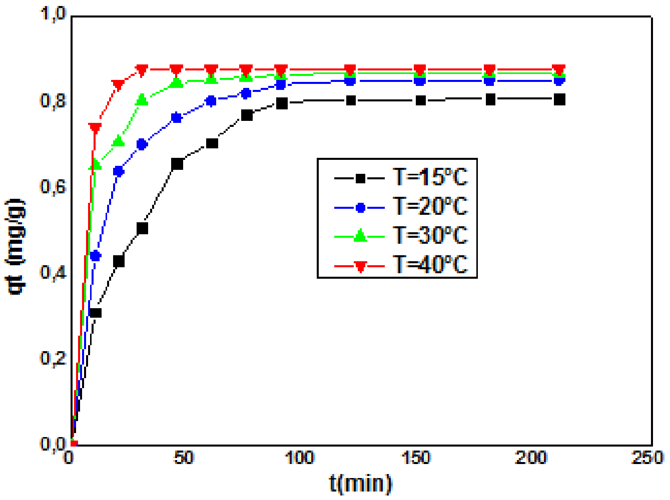

Fig.5. The effect of temperature on the removal of indigo carmine by CAG for different time intervals (C_0=35mg/l, m=1g, V=200 rpm).

4. ADSORPTION ISOTHERM STUDY

The adsorption isotherm can describe the distribution of dye between the solid phase and the solution at persistent temperature when the equilibrium was reached. The Langmuir, Freundlich, Liu, Khan and Redlich Peterson models were applied to fit the equilibrium data. So in order to predict the optimum adsorption isotherm in this study, we used the non-linear regression method as one of the most used and adequate methods for best fitting [23,24].

The statistical functions errors were used to compare the isotherm equations by judging most widely types of functions (Residual sum of squares, reduced chi-squared, standard deviation, coefficient of determination, adjusted R-squared), it was expressed as follows (table 1) [25-27].

Table.1. Lists of different error functions and their expressions

Error function	Expression	Eq
Residual sum of squares (RSS)	$\mathrm{RSS}=\sum_{i=1}^{N}\left(q_{i,observed}-q_{i,calc}\right)^2$	(3)
Reduced Chi-squared (χ^2_{red})	$\chi^2_{red}=\sum_{i=1}^{N}\frac{\left(q_{i,observed}-q_{i,calc}\right)^2}{N-P}$	(4)
Standard deviation (SD)	$\mathrm{SD}=\sqrt{\left(\frac{1}{N-P}\right)\sum_{i=1}^{N}\left(q_{i,observed}-q_{i,calc}\right)^2}$	(5)
Coefficient of determination (R^2)	$R^2=\left[\frac{\sum_{i=1}^{N}\left(q_{i,observed}-\bar{q}_{observed}\right)^2-\sum_{i=1}^{N}\left(q_{i,observed}-q_{i,calc}\right)^2}{\sum_{i=1}^{N}\left(q_{i,observed}-\bar{q}_{observed}\right)^2}\right]$	(6)
Adjusted R squared (R^2_{ajd})	$R^2_{adj}=1-\left(1-R^2\right)\left(\frac{N-1}{N-P-1}\right)$	(7)

4.1 Langmuir isotherm

The Langmuir isotherm characterized by monolayer adsorption is dependent on the assumption that adsorption takes place at specific homogeneous locations in the adsorbate [28]. The Langmuir equation is written as follows (Eq.8):

$$q_e=\frac{q_m K_L C_e}{1+K_L C_e} \quad (8)$$

4.2 Freundlich isotherm

The Freundlich isotherm model is an empirical equation used to describe the heterogeneous system it can be expressed by Eq.9 [29]:

$$q_e = K_F C_e^{1/n} \tag{9}$$

4.3 Liu isotherm

The Liu isotherm model is a combination of the Langmuir and Freundlich isotherm models, but the monolayer assumption of Langmuir model and the infinite adsorption assumption that originates from the Freundlich model are discarded. The Liu model predicts that the active sites of the adsorbent cannot possess the same energy. Therefore, the adsorbent may present active sites preferred by the adsorbate molecules for occupation, however, saturation of the active sites should occur unlike in the Freundlich isotherm model. Eq. (10) defines the Liu isotherm model [30-32]:

$$q_e = \frac{q_{max}(K_g C_e)^{n_L}}{1+(K_g C_e)^{n_L}} \tag{10}$$

n_L could take any positive value

4.4 Khan isotherm

Khan isotherm model developed for demonstrating the equilibrium adsorption data, it is generally applicable for pure solution it is expressed as [33,34] :

$$q_e = \frac{q_m b_k C_e}{(1+b_K C_e)^{ak}} \tag{11}$$

4.5 Redlich Peterson isotherm

Redlich Peterson model it can be employed in heterogeneous or homogenous systems, which united both Langmuir and Freundlich isotherms, whith three parameters isotherm which is denoted as follows [35] :

$$q_e = \frac{K_R C_e}{1 + a_K C_e^g} \tag{12}$$

The non-linear fitting values of the two and three parameter isotherm models using the five error function are summarized in table 2 and the results of the experimental data can be seen in fig.6. As depicted in the table2, the Langmuir's constant K_L increase as temperature increasing which allude to the strong interaction between the adsorbate and adsorbent with a specific homogeneous location. The n_F values of Freundlich isotherm were found >1 reveals the favorable adsorption of indigo carmine onto activated carbon, and the adsorption capacity K_F increase with increasing the solution temperature indicating that the process adsorption can be endothermic once again. Furthermore, it can be concluded with looking at the rest of results that the Redlich Peterson is adequately fitted better than Khan isotherm with the exponent g values are approximately equal to 1 ,which implies that the model revealed tending toward Langmuir isotherm and not Freundlich. According to the error function calculation, we can deduce that the Liu isotherm model is perfectly described the equilibrium data with R^2_{adj}=0,998-0,9997-0,9837 at all the three studied temperatures when comparing with the other isotherm models . For this, we can conclude that the three parameters model fitted better the adsorption of indigo carmine onto activated carbon rather than the two parameters models. To determine the efficiency of activated carbon to remove indigo carmine, a comparison with some latest literature works was realized according to the value of monolayer adsorption capacity (qm). According to the comparison study, the value obtained from this work may be estimated that granular activated carbon is a promising adsorbent to remove indigo carmine when compared to coal fly ash(1.48 $mg.g^{-1}$) , zeolite from fly ash(1.23 $mg.g^{-1}$) [36] and Palm Wood Cellulose(5.3910 $mg.g^{-1}$)[37].

Table 2.Values of the two and three parameter isotherm models for the adsorption of indigo carmine on activated carbon at different temperature

T(K)	**293**	**298**	**303**
		Langmuir	
K_L	1.65	2.37	10.2
q_m	3.72	4.13	4.26
RSS	0.205	0.00217	0.248
χ^2_{red}	0.0410	$4.34x10^{-4}$	0.0495
SD	0.205	0.0208	0.222
R^2	0.9768	0.9998	0.9742
R^2_{ajd}	0.9722	0.9997	0.9691
		Freundlich	
K_F	2.45	2.79	4.19

n	5.99	3.48	3.94
RSS	0.510	0.0986	0.465
χ^2_{red}	0.102	0.0197	0.0929
SD	0.319	0.140	0.305
R^2	0.9423	0.9895	0.9571
R^2_{ajd}	0.9307	0.9874	0.9421
Liu			
K_g	1.29	2.39	10.1
q_{max}	3.36	4.10	3.54
n_L	2.49	1.01	2.67
RSS	0.0117	0.00214	0.104
χ^2_{red}	0.00292	$5.35x10^{-4}$	0.0261
SD	0.0540	0.0231	0.162
R^2	0.9987	0.9998	0.9892
R^2_{ajd}	0.9980	0.9997	0.9837
Khan			
b_K	0,5670	2,21177	2,87613
q_m	7,1319	4,32459	10,6448
a_K	1,3191	1,02003	1,62552
RSS	0,0928	0,00199	0,1682
χ^2_{red}	0,0232	$4{,}97\ x10^{-4}$	0,04205
SD	0,1523	0,0222	0,2050
R^2	0,9895	0,9997	0,9825
R^2_{ajd}	0,9842	0,9996	0,9737
Redlich Peterson			
K_R	3,4779	9,52491	26,60789
α_R	0,5648	2,27463	6,76943
g	1,2274	1,01204	1,31907
RSS	0,0798	0,00203	0,1602

χ^2_{red}	0,0199	5,08 x10^{-4}	0,04005
SD	0,1412	0,0225	0,2001
R^2	0,9909	0,9997	0,9833
R^2_{ajd}	0,9864	0,9996	0,9750

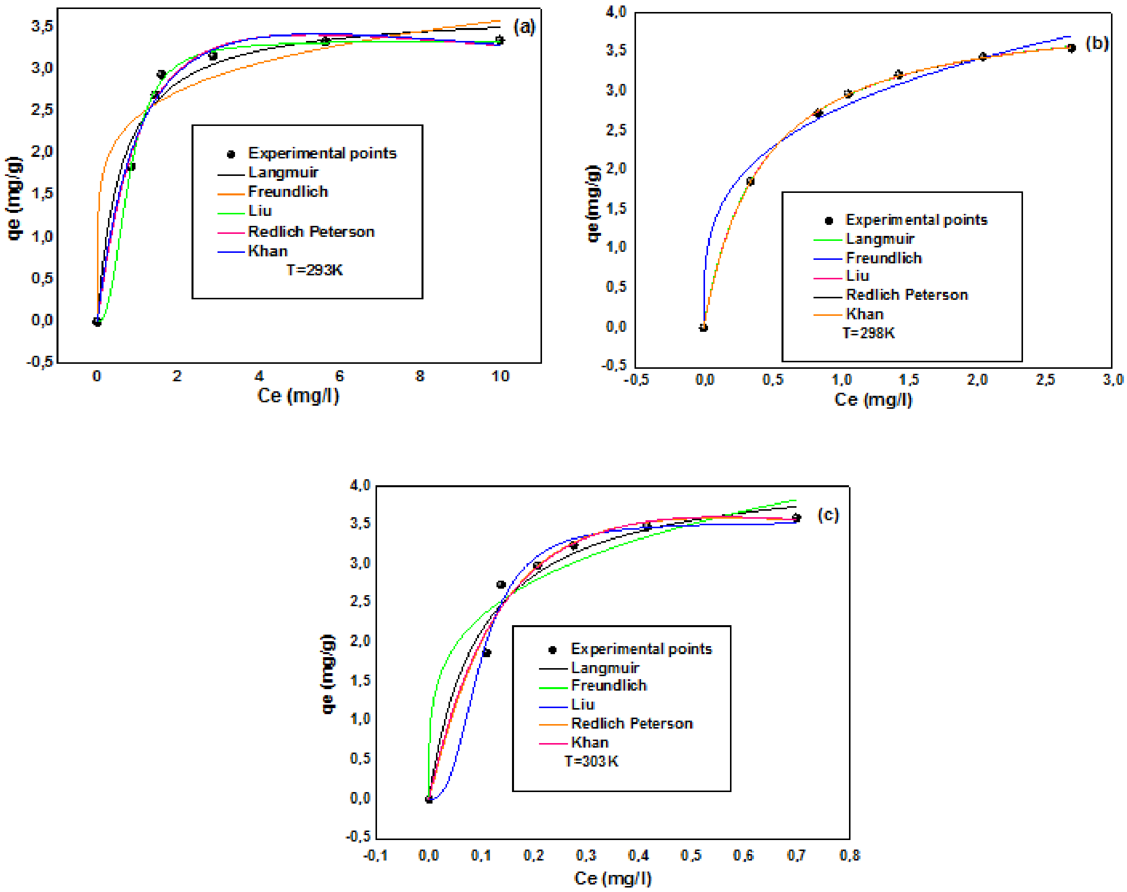

Fig.6. The curves of the five nonlinear isotherm models fitted to experimental adsorption (a) at 293K, (b) at 298K and (c) at 303K

5. KINETICS STUDIES

In order to evaluate the mechanism on the adsorbate and adsorbent, four famous different kinetic model were studied, Pseudo first order, Pseudo-second order, Avrami and Elovich [38].

5.1 Pseudo-first-order kinetic model

For the pseudo first order: the adsorption rate constant k_1 is given by the following relation [39]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (13)$$

Integrating (Eq13.) with the boundary conditions, t=0 to t and from 0 to q_t leads to non-linear form:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (14)$$

5.2 Pseudo-second-order kinetic model

The pseudo-second-order model depends on the amount of solute adsorbed on the surface of the adsorbent and the amount adsorbed at equilibrium. The pseudo-second-order model proposed by Blanchard , developed by Ho it can be represented in the following form [40]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (15)$$

The integration of Eq. (15) leads to the non-linear form:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (16)$$

The initial rate of adsorption k_2 can be written as (equation17):

$$h_O = k_2(q_e)^2 \quad (17)$$

5.3 Avrami kinetic model

The avrami exponential model is an adaptation of kinetic thermal decomposition modeling it is expressed as [41]:

$$q_t = q_e\left(1 - \exp\left(-(k_{AV}.t)^{nAV}\right)\right) \quad (18)$$

5.4 Elovich model

This model generally satisfied in chemical adsorption kinetics and it is useful when the adsorbing surface is heterogeneous. The equation used is shown bellow [42,43] :

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (19)$$

Integrating equation 19 by applying the boundary conditions; qt = 0 at t= 0 and qt = qt at t= t to gives Eq. (20):

$$q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln(t) \tag{20}$$

The graphical presentation for kinetic adsorption of indigo carmine dye onto CAG is presented in figure7, and the fitting parameters of the kinetics models were summarized in table 3. From these results, we can conclude that the Avrami fractionary kinetic model shown a good fitting to the experimental data (low value of SD and high value of R^2_{adj}).The adsorption capacity at equilibrium (0.619 mg.g^{-1}) is fairly consistent to experimental value (0.620 mg.g^{-1}). The order of kinetic model (n_{AV}) is 1.24. This value is between 1 (pseudo-first order) and 2 (pseudo-second-order). Therefore, a fractional value of the reaction order (n_{AV} = 1.24) can be attributed to a change in the kinetics of the adsorption from the pseudo-first order to the pseudo-second order during the contact of the adsorbate with the adsorbent [44]. The low value of R^2_{adj} obtained from Elovich kinetic model implies that the mechanism of the IC adsorption onto CAG adsorbent did not follow the chemisorption process.

Table 3.The results of kinetic parameters for the adsorption of IC onto activated carbon

Kinetic models and its parameters			
Values			
	qe(exp)		0.620
Pseudo-first order		**Elovich**	
k_1	0.0597	α	0.353
q_e(cal)	0.625	β	9.62
RSS	0.00291	RSS	0.0366
χ^2_{red}	2.91x10^{-4}	χ^2_{red}	0.00366
SD	0.0170	SD	0.0605
R^2	0.9931	R^2	0.9139
R^2_{adj}	0.9924	R^2_{adj}	0.9051
Pseudo-second order		**Avrami**	
k_2	0.128	q_e(cal)	0.619
q_e(cal)	0.688	k_{AV}	0.0590
h_0	0.0607	n_{AV}	1.24
RSS	0.0142	RSS	0.00137

χ^2_{red}	0.00143	χ^2_{red}	1.52×10^{-4}
SD	0.0378	SD	0.0123
R^2	0.9663	R^2	0.9968
R^2_{adj}	0.9629	R^2_{adj}	0.9960

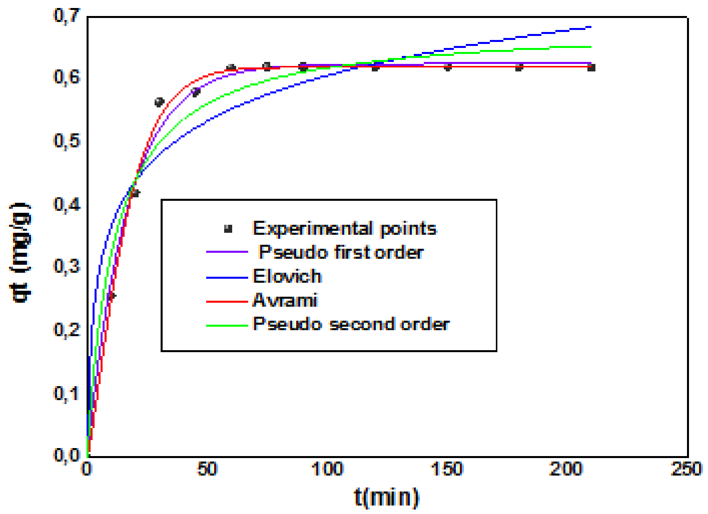

Fig.7. Nonlinear plot of Pseudo first order, Pseudo second order, Elovich, and Avrami kinetic model for the adsorption of IC onto activated carbon at T=293K

6. THERMODYNAMIC STUDY

As reported previously the temperature was an important factor in the adsorption process, in order to determine the thermodynamic nature of CAG adsorbent for IC adsorption, different parameters estimated such as the standard free energy change ΔG°, the standard enthalpy ΔH° and the standard entropy ΔS° it can be calculated from [45] :

$$\Delta G° = -RTLnK \quad (21)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (22)$$

$$LnK = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (23)$$

A plot log K Vs. (1/T) is given straight line, ΔH°and ΔS° can be determined from intercept and slope, respectively. From the following results which is presented in table 4, the positive values of ΔS° indicates the increased randomness of the system solid-solution interface during the adsorption process [46], the negative values of ΔG° suggest that the adsorption of indigo carmine onto activated carbon is a spontaneous processand the spontaneity increases with temperature.The decrease in ΔG° with temperature implies more efficient adsorption at higher temperatures.The positive values of ΔH° reveals the endothermic nature of indigo carmine adsorption on activated carbon at 293-303°K [47,48].

Table 4. Thermodynamics parameters of IC adsorption onto CAG

T(K)	293	298	303	293	298	303
Isotherm	**Langmuir**			**Liu**		
ΔS^0 ($J.K^{-1}.mol^{-1}$)	460.00			518.15		
ΔH^0 ($KJ.mol^{-1}$)	134.00			151.54		
ΔG^0 ($KJ.mol^{-1}$)	-1.22	-2.14	-5.85	-0.620	-2.16	-5.83

7. CONCLUSION

This study demonstrated the effectiveness of commercial activated carbon in the removal of indigo carmine dye in an aqueous medium. The influence of the parameters related to the operating conditions was examined. The plot of the adsorption isotherms shows that the Liu model perfectly describes the adsorption of indigo carmine on activated carbon with R^2adj=0,998-0,9997-0,9837 over the studied temperature (T=293,298,303K). The kinetic study shows that the adsorption mechanism can be described by a kinetic of the Avrami model. The thermodynamic parameters obtained indicate that the adsorption of indigo carmine dye on granular activated carbon is endothermic, spontaneous and increasing the randomness during the adsorption process.

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