

## Adsorption of Organic Dyes onto Commercial Activated Carbon by Using Non-linear Regression Method

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### Abstract

The present paper intends to appraise the influencing operative variable on the adsorption efficiency of two organic dyes namely Erythrosine and Brilliant green on activated carbon in aqueous solution. The experimental data at equilibrium were studied through the non-linear regression of Langmuir, Freundlich and Liu isotherm models. Collected data and obtained results seems to fit well with the Liu model for both dyes with  $R^2_{adj}$  values closer to one and lower values of SD. The kinetic behaviors of solute adsorption were respectively employed by using different existing models, Pseudo-first, Pseudo-second order, General order, Avrami and Elovich equation. Findings results showed that General order had more conformity compared with the others, for Brilliant green with  $R^2_{adj}=0.9949$  and Avrami kinetic model for Erythrosine with  $R^2_{adj} = 0.9956$ . According to the calculated thermodynamic parameters the adsorption process of the Erythrosine dye is endothermic and spontaneous process in nature ( $\Delta H^0=41.428-41.459\text{KJ/mol}$ ) and non-spontaneous for the Brilliant green dye ( $\Delta H^0=80.409-54.955\text{KJ/mol}$ ) over the studied temperatures (293K-303K).

**Keywords:** Erythrosine; Brilliant green; Activated carbon; Isotherm; kinetic; Non-linear regression.

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### 1. Introduction

Discharging of noxious residues from dyeing industries into environment leads to a serious risk to living aquatic organisms and human health. The existence of an extremely small concentration of dyes in water can be perilous because most of them are poisonous and carcinogenic. Furthermore, some of them have complicated aromatic structures, which render

them more stable and difficult to remove (Ghaedi *et al.*, 2018; Karimifard and Moghaddam, 2018; Zazouli *et al.*, 2016; Rahman *et al.*, 2018). Consequently, their discoloration and reduce from industrial effluents before discharge into a range of receiving environments is exceedingly vital and continues to be problematic (Uday *et al.*, 2017; Uruj *et al.*, 2016; Heibati *et al.*, 2015). Erythrosine and brilliant green are some of the prevalent synthetic dyes, which are used in the

cloth industry, pharmaceutical, cosmetic, and food. These dyes are regarded as an irritant of the skin, eye burns, and gastrointestinal symptoms with nausea, vomiting, diarrhea. It may also cause learning difficulties (hyperactivity) and sensitivity to light (Al-Degs *et al.*, 2012; Karimi *et al.*, 2016; Salem *et al.*, 2015; Kumar *et al.*, 2014; Roosta *et al.*, 2014). There are many dyes removal techniques as ion exchange, electro-coagulation, coagulation-flocculation, oxidation, reverse osmosis, adsorption, photocatalytic degradation, and nano-filtration. Nevertheless, adsorption on activated carbon is regarded as an efficient and popular approach largely adopted for industrial treatment. The main advantage of this method is removing a wide range of toxic effluents in a single run, which lead to high quality of treated wastewaters in a short time with flexibility in design and operation (Abid *et al.*, 2012; Li *et al.*, 2017; Doczekalska *et al.*, 2018; Mukhlis *et al.*, 2016; Castañeda - Díaz *et al.*, 2017; Deng *et al.*, 2015; Carneiro *et al.*, 2016; Wawrzkiwicz *et al.*, 2015; Buscio *et al.*, 2016). Activated carbon is one of the best and effective adsorbents used for many applications due to a higher degree of porosity and extended surface area, leading to a high adsorbent capacity (Corda and Srinivas, 2018; Di Biase and Sarkisov, 2015; Anisuzzaman *et al.*, 2015). In order to estimate the efficiency in the removal of erythrosine and brilliant green onto granular activated carbon, stational optimization of the influential variables (initial concentration, agitation speed, pH and temperature), was well evaluated and elucidated using batch method experiments. Modeling of kinetic adsorption and isotherm parameters were also assessed to understand the mechanism of adsorption between the adsorbates and adsorbent.

## 2. Materials and methods

### 2.1 Adsorbent

The specific surface area of granular activated carbon (CAG) of vegetable origin which is produced by Prolabo with a particle size < 3 mm, carried out in a Micromeritics ASAP 2020 with nitrogen at 77K exhibits a hysteresis for which the desorption branch joins the adsorption branch for a relative pressure equal

to 0.42 (Figure 1). This hysteresis is significant in the presence of mesoporous (type IV isotherm) (Thommes *et al.*, 2015; Jayaraman, 2017). The CAG had specific area equal to  $\sim 988 \text{ m}^2/\text{g}$  determined by plotting the curve  $\frac{P_i}{V_{ads}(1-P_i)}$  versus  $P_r$  (Pression). with the pore diameter of  $36 \text{ \AA}^\circ$  (pore diameter greater than  $20 \text{ \AA}^\circ$ ), thus, it has a mesoporous texture.

### 2.2 Selected dyes

Two organic dyes produced from Merck were chosen as model adsorbates. Brilliant green is one of common basic dyes in the class of triarylmethane dye (sulfate of di-(p-diethylamino) triphenyl carbonyl anhydride) and Erythrosine which is an organ-iodine compound derived from fluorine presented under the form of disodium salt of 2, 4,5,7 tetraiodfluorescein were chosen because of their different structures (Table 1 and Figure 2).

The determination of the concentration of the molecules adsorbates in aqueous solution was measured through a molecular absorption spectro-photometry (Spectronic70 Spectro-photometer). It has been calculated by referring to the calibration curve obtained by linear fitting from test solutions at a wavelength ( $\lambda_{\text{max}}$ ) corresponding to the maximum absorbance for each dye (Table 1 and Figure 3). Eq. 1 was used to calculate the adsorption quantity of dyes adsorbed on granular activated carbon at the time t (Manera *et al.*, 2018).

$$q_t = \frac{C_0 - C_t}{m} \times v \quad \text{Eq. 1}$$

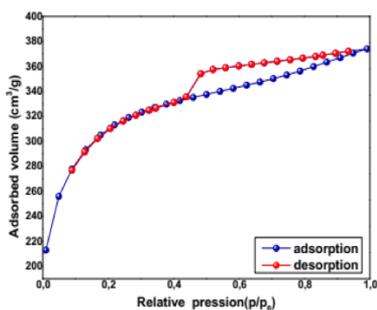
The amount adsorbed at Eq. 1,  $q_e$ , was calculated using Eq. 2 (Gautam *et al.*, 2015).

$$q_e = \frac{C_0 - C_e}{m} \times v \quad \text{Eq. 2}$$

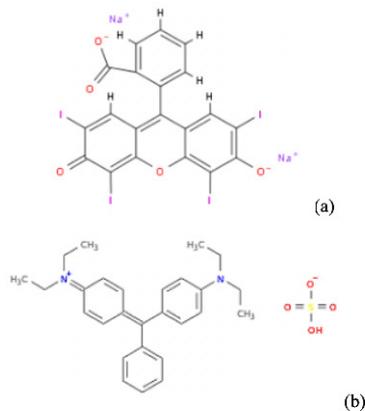
Where,  $q_t$ : quantity of adsorbate adsorbed at time t (mg/g),  $C_0$  and  $C_t$ : initial and remaining concentration (mg/l) of dye in solution respectively,  $q_e$ : dye adsorbed quantity (mg/g) per unit mass of activated carbon at equilibrium,  $C_e$ : remaining concentration (mg/L) of dye at equilibrium V: the volume (L) of dye solution and m is the weight (g) of the activated carbon.

**Table 1.** Main characteristics of dyes used with different forms.

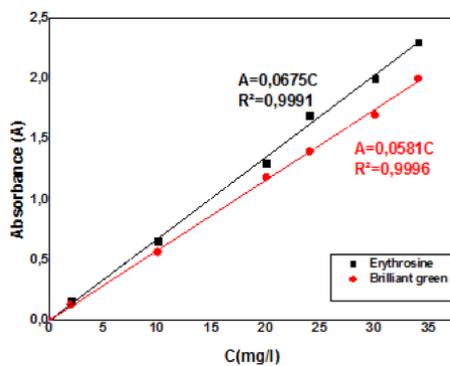
Dye	Brilliant green	Erythrosine
C.I.name	C.I. 42040	C.I. 45430
Molecular Formula	$C_{27}H_{34}N_2O_4S$	$C_{20}H_6I_4Na_2O_5H_2O$
Molecular weight (g/mol)	482.64	897.88
$\lambda_{max}$ (nm)	623 nm	527 nm



**Figure 1.** Isotherm adsorption-desorption of nitrogen on commercial activated carbon.



**Figure 2.** Chemical structure of Erythrosine (a) and Brilliant green (b).



**Figure 3.** Calibration curves for Erythrosine and Brilliant green solutions.

### 3. Results and discussion

#### 3.1 SEM micrographs

The external surface topography of CAG is identified by SEM scanning electron microscope (Joel-JSM-6360L V) scanning electron microscope, and the results are showed in figure 4. As shown the surface of CAG had considerable numbers of pores where dyes can be caught and adsorbed. The microscope analysis of CAG sample before adsorption shows specific dark spots, revealing a big eventuality, for adsorbing dye molecules in the pores. Apparent reduction of dark spots can be noticed in Figure 4 (B and C) deduced as a sign of presence of dyes on the surface of CAG.

#### 3.2 Effect of initial concentration on adsorption ability

The effect of the initial concentration on adsorption ability of both dyes was inspected with varying the concentration between 15 and 45 mg/l. The analysis curves are shown in Figure 5 demonstrates that the raise of initial of initial concentration leads to an increase of adsorbed dyes. As an indication, the amount of adsorbed dyes increased from 0.373 to 1.10 mg/g in case of erythrosine and from 0.371 to 1.09 mg/g in case of brilliant green during a contact time of 210 min, this might be due to an increase in the number of collisions between the adsorbates and the adsorbent, hence enhancing the adsorption rate. Similar conclusions on the effect of adsorbate concentration on the removal behavior have been proposed by (Albroomi *et al.*, 2016) for the adsorption of tartrazine by activated carbon prepared from apricot stones.

#### 3.3 Effect of agitation speed on adsorption ability

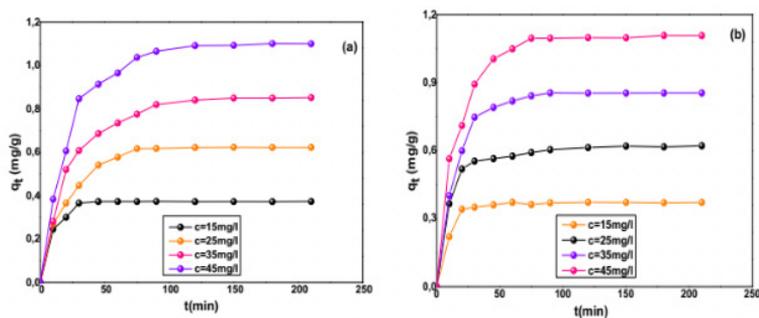
The agitation speed is essential parameter to ensure the transfer of solute molecules to the adsorbent. The curves in Figure 6 illustrate the consequence of agitation speed on dyes elimination of erythrosine and brilliant green in the range of 60 to 275 rpm. It is apparent in the figure that the increase of agitation speed leads to an increase of adsorbed dyes. As an indication, the quantity of erythrosine adsorbed increased from 0.76 to 0.86 mg/g and that of brilliant green from 0.77 to 0.87 mg/g when

the agitation speed varies from 60 to 275 rpm during a contact time of 210 min. Because of the fact that the raise in the agitation speed provides good homogenization of the solution in order to achieve the equilibrium state and leads to a decrease in diffusion layer thickness surrounding the adsorbent surface (Prashanthi *et al.*, 2017). The increase of the adsorption rate with the agitation speed was also reached for the adsorption of 4-chlorophenol on granular activated carbon (Kusmieriek and Swiatkowski, 2015) as well as the adsorption of red violet on montmorillonite clay (Fil *et al.*, 2014).

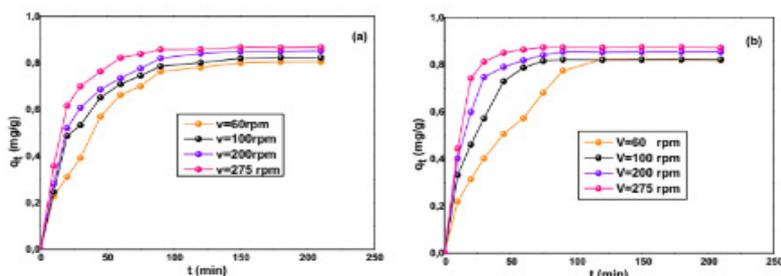
#### 3.4 Effect of initial pH on adsorption ability

As well-known, the pH is one of an operative parameter influenced in practically the adsorption capacity because it plays a primary role to the adjustment of the adsorption facility of adsorbent, controls the charge in surface of the adsorbent and affects the ionization level of the dye in the solution. To evaluate the pH effectiveness on dyes removal by CAG, a series of experiments at different pH between 3 and 11 was conducted. From Figure 7, it was observed that the pH has an obvious influence in the extent of adsorption.

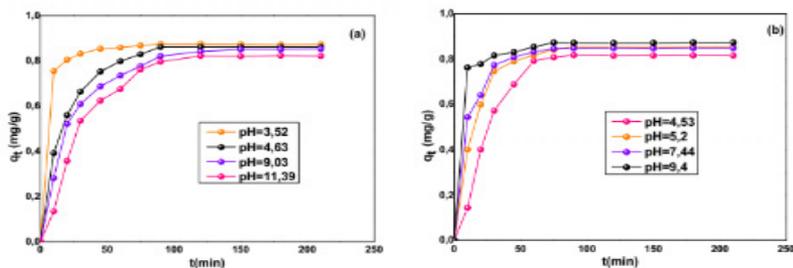
The adsorption capacity of brilliant green (Figure 7-b) was found favorably increased at increasing values of pH which is associated with the negative charge on CAG surface and the positive charge of brilliant green (cationic dye). At acidic pH values, the number of positively charged sites on the adsorbent surface increased which enhance the positively charged of brilliant green through an electrostatic force of repulsion which caused a diminished in the removal efficiency. A similar behavior was studied on the removal of cationic dye on sepiolite and malachite green on modified (MIL-101-SO<sub>3</sub>H) (Demirbas *et al.*, 2014; Luo *et al.*, 2017). Contrarily when the pH of erythrosine dye solution becomes low (pH≤4) the adsorption capacities increased (Figure 7-a). The presence of H<sup>+</sup> ions as functional group at low pH increases the number of positive charges of adsorbent in spite of the negative charge of the dye (anionic dye), indicating an electrostatic attraction between the adsorbate and adsorbent with a highest



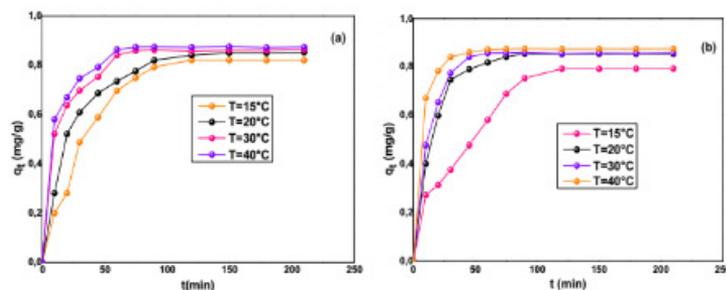
**Figure 5.** Effect of initial concentration on adsorption ability of Erythrosine (a) and Brilliant green (b). Experimental conditions:  $m=1000$  mg,  $v=200$  rpm,  $T=293$ K,  $pH=9,03, 5,2$  and  $V=25$ ml.



**Figure 6.** Effect of agitation speed on adsorption ability of Erythrosine (a) and Brilliant green (b). Experimental conditions:  $m=1000$  mg,  $C_0=35$  mg/L,  $T=293$ K,  $pH=9,03, 5,2$  and  $V=25$ ml.



**Figure 7.** Effect of pH values on adsorption ability of Erythrosine (a) and Brilliant green (b). Experimental conditions:  $m=1000$  mg,  $C_0=35$  mg/L,  $v=200$  rpm,  $T=293$ K and  $V=25$ ml.



**Figure 8.** Effect of solution temperature on adsorption ability of Erythrosine (a) and Brilliant green (b). Experimental conditions:  $m=1000$  mg,  $C_0=35$  mg/L,  $v=200$  rpm,  $pH=9,03, 5,2$  and  $V=25$ ml.

value of adsorbed quantity at pH 3.52 for 60 min contact time. At higher pH (pH≥9), the presence of OH- on the surface of adsorbent might not support the sorption of anionic dye. The similar trends were seen for removal of RB5 on DMAC16, acid red 57 on calcined-alunite and brilliant blue R using Amino-Functionalized Organosilane (Erdem et al., 2016 ;Tunali et al., 2016; Saputra et al., 2017).

### 3.5. Effect of solution temperature on adsorption ability

The temperature was an influencing parameter to understand the bonding between the adsorbent surface and substance adsorbed; it was evaluated within the range 288K to 313K. According to the curves of Figure 8, the equilibrium time increases as temperature increases shifting from 120 min for T=288K to 50 min for 313K. This may be justified by increasing the particles motion and hence promoting their incursion into the pores of the activated carbon. Additionally, the solution viscosity reduces by rising the temperature leading to an increase in the rate of diffusion of the adsorbates across the outside boundary layer, which in turn, enhances the adsorption ability (El Haddad et al., 2013).

## 4. Determination of adsorption isotherm parameters

A nonlinear form of adsorption isotherms were simulated by using several models, such as: Langmuir, Freundlich and Liu for describing the partition of dyes between solid phase and the solution, in order to discuss the experimental characteristics of the adsorption isotherms.

### 4.1 Langmuir isotherm

The model is depended on the following assumptions: (Gurdeep ,2000; Li et al., 2012) homogeneous sites within the adsorbent (all binding sites having the same energy), Absence of Interactions between the adsorbed molecules, All adsorption take place through the same mechanism, Formation of an adsorbate monolayer coverage the surface of the adsorbent, Each site can react only with one adsorbate species.

The Langmuir equation gives as Eq. 3.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Eq.3}$$

Where,  $q_e$  is the quantity of adsorbed dye per unit activated carbon mass (mg/g),  $q_m$ : utmost adsorption capacity (mg/g),  $K_L$ : equilibrium constant related to affinity of binding sites (L/mg) ,  $C_e$ : residual concentration of dye at equilibrium (mg/L).

### 4.2 Freundlich isotherm

Freundlich gives an experiential expression used to explicate the adsorption properties over different surfaces. It is often conveyed by the Eq. 4 (Freundlich, 1906):

$$q_e = K_F C_e^{1/n} \quad \text{Eq.4}$$

Where,  $K_F$ : Partition coefficient constant of Freundlich in equilibrium (mg<sup>(1-n)</sup>L<sup>n</sup>/g),  $n_F$ : Intensity and capacity of adsorption (Without units).

### 4.3 Liu isotherm

The Liu model can be regarded as an arrangement of both Langmuir and Freundlich isotherms without assumption, in general is based on the fact that the binding sites are energetically different. Consequently, the adsorbent active sites may exhibit different affinities towards adsorbate molecules; however, saturation of the active sites should occur in a different manner of that of the Freundlich model. Eq. 5 expressed the mathematical relation of Liu isotherm model (Liu et al., 2003; Bergmann et al .,2015; Dos Santos et al ., 2015):

$$q_e = \frac{q_{\max} (K_g C_e)^{n_L}}{1 + (K_g C_e)^{n_L}} \quad \text{Eq.5}$$

Where  $K_g$ : equilibrium constant of Liu isotherm (L/mg),  $n_L$ : exponent of the Liu equation (dimensionless).

## 5. Error functions

In recent decades the parameters of the preceding isotherms estimated by linear regression, which is widely used as one of the most common method for best fitting. Most

of works was based on the choice of a mathematical model on the value of R<sup>2</sup> (correlation coefficient). However, the use of only one R<sup>2</sup> may not be sufficient for comparing the goodness of fit. This is because of the distribution of error changes either the worst or the best and fit distortion (Foo *et al.*, 2010). For this, we use the nonlinear regression in this study to minimize errors that may be introduced between the predicted data and experimental color removal by subjecting on the convergence criteria as an adequate method (Belhachemi and Adoun, 2011). With a comparison of two previous methods, statistically, the more appropriate and estimate method obtained by nonlinear regression model (Srensek-Nazzal *et al.*, 2015; Özdemir and Önal, 2013; Boulinguez *et al.*, 2008, Largitte and Pasquier, 2016). Different type of error functions have been used for testing the result of a regression model for residue analysis. In this context, we chose five types of statistical functions among the most widely used in such studies, which are represented by Eqs.6 to 10, respectively (Machado *et al.*, 2011).

5.1 Residual sum of squares (RSS)

$$RSS = \sum_{i=1}^n (q_{i,observed} - q_{i,calc})^2 \quad \text{Eq. 6}$$

5.2 Reduced Chi-squared (X<sup>2</sup><sub>red</sub>)

$$X^2_{red} = \sum_{i=1}^m \frac{(q_{i,observed} - q_{i,calc})^2}{N - P} \quad \text{Eq.7}$$

5.3 Standard deviation (SD)

$$SD = \sqrt{\left(\frac{1}{N - P}\right) \sum_{i=1}^n (q_{i,observed} - q_{i,calc})^2} \quad \text{Eq.8}$$

5.4 Coefficient of determination (R<sup>2</sup>)

$$R^2 = \frac{\sum_{i=1}^n (q_{i,observed} - \bar{q}_{observed})^2 - \sum_{i=1}^n (q_{i,observed} - q_{i,calc})^2}{\sum_{i=1}^n (q_{i,observed} - \bar{q}_{observed})^2} \quad \text{Eq.9}$$

5.5 Adjusted R-squared

$$R^2_{adj} = 1 - (1 - R^2) \left( \frac{N - 1}{N - P - 1} \right) \quad \text{Eq.10}$$

Where, N: total number of experimental

data and P: the number of parameters of the fitted model, R<sup>2</sup>: coefficient of determination.

The most suitable model should have a minimum value of SD and R<sup>2</sup><sub>adj</sub> equals almost one (Bergmann and Machado, 2015). The results of modeling data for both dyes onto activated carbon are summarized up in Tables 2. We note that the Langmuir constant K<sub>L</sub> increases with increasing temperature for both dyes. As the value of K<sub>L</sub> measures the intensity of adsorption, we deduce that affinity between the adsorbates and activated carbon increases as the temperature elevated from 293K to 303 K. Comparing the Adjusted R- squared values (R<sup>2</sup><sub>adj</sub>) between the erythrosine and brilliant green dye, the results showed that the Langmuir model is favorably adapted for adsorbed erythrosine than brilliant green dye at different ranges of temperature.

The Freundlich exponent n is bigger than 1, indicating a favorable adsorption of erythrosine and brilliant green at experimental conditions (El-Sayed *et al.*, 2014). The error calculations show that the Liu isotherm model turns out to be suitable for both dyes compared with the two other models (Liu>Langmuir>Freundlich). The Liu model is well adapted to describe the adsorption of erythrosine and brilliant green on activated carbon.

The peak adsorption capacity of brilliant green and erythrosine dyes by other potential adsorbents are given in Table 3. As depicted, the q<sub>max</sub> of brilliant green onto granular activated carbon was higher value than the other values and for erythrosine dye, it was average value compared to the adsorbents listed. However, the entire of modeling results proved that the CAG fits very well as promising adsorbent on cationic and anionic dyes removal.

**6. Adsorption kinetics modelling**

A number of adsorption kinetic was evaluated to optimize the adsorption mechanism pathways, with examining the rate of adsorption procedure, several models in this study was undertaken to investigate the kinetic data.

6.1 Pseudo-first-order kinetic model

The Lagergren model was discovered initially as non-reversible equation (Lagergren.,

**Table 2.** Non-linear regression parameters of adsorption isotherm models of Erythrosine and Brilliant green on activated carbon with error analysis.

	Erythrosine			Brilliant green		
T(K)	293	298	303	293	298	303
<b>Langmuir</b>						
$K_L$	1.0847	1.2077	1.9052	0.1404	0.2032	0.4182
$q_m$	4.2869	4.7727	4.4357	5.5442	5.4057	4.5535
RSS	0.0228	0.0639	0.1040	0.2028	0.0589	0.1741
$X^2_{red}$	0.0045	0.01279	0.0208	0.0405	0.0117	0.0348
SD	0.0675	0.1130	0.1442	0.2014	0.1085	0.1866
$R^2$	0.9975	0.9932	0.9890	0.9757	0.9931	0.9802
$R^2_{adj}$	0.9970	0.9918	0.9868	0.9708	0.9918	0.9762
<b>Freundlich</b>						
$K_F$	2.2520	2.5814	2.8242	1.0651	1.2412	1.7380
$n$	3.0257	2.7154	3.2393	2.0822	2.0905	2.9360
RSS	0.0898	0.1968	0.2743	0.3053	0.1295	0.3373
$X^2_{red}$	0.0179	0.0393	0.0548	0.0610	0.0259	0.0674
SD	0.1340	0.1982	0.2340	0.2471	0.1609	0.2597
$R^2$	0.9902	0.9790	0.9709	0.9634	0.9849	0.9616
$R^2_{adj}$	0.9882	0.9749	0.9651	0.9561	0.9819	0.9540
<b>Liu</b>						
$K_g$	1.2538	1.5988	2.1998	0.2391	0.3321	0.5037
$q_{max}$	3.9025	3.8059	3.6434	3.4672	3.9698	3.4808
$n_L$	1.2657	1.8192	2.0645	3.1313	1.6790	2.6407
RSS	0.017	0.0020	0.0043	0.01361	0.0266	0.0055
$X^2_{red}$	0.0042	5.01x10 <sup>-4</sup>	0.0010	0.0034	0.0066	0.0013
SD	0.0651	0.0223	0.0328	0.0583	0.0815	0.0372
$R^2$	0.9981	0.9997	0.9995	0.9983	0.9969	0.9993
$R^2_{adj}$	0.9972	0.9996	0.9993	0.9975	0.9953	0.999

1898), and validated in general, in the first minutes of the adsorption phenomena (Eq.11)

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{Eq.11}$$

Where,  $k_1$ : rate constant of pseudo-first-order sorption ( $\text{min}^{-1}$ ). Equation (12) can be presented by:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{Eq.12}$$

### 6.2. Pseudo-second-order kinetic model

This model is described by Ho and Mckay it is valid for a wide range of time and requires a chemisorption mechanism (Ho and Mckay, 1999). It expression as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{Eq.13}$$

The integration of Eq. (13) leads to the non-linear form:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{Eq.14}$$

The advantage of using the non-linear form lies directly on the fact that we do not need to know the equilibrium capacity  $q_e$  from experience, since it can be determined from the model. This makes it possible to determine  $K_2$  and the initial rate of adsorption Eq. (15).

$$h_0 = K_2(q_e)^2 \quad \text{Eq.15}$$

Where,  $K_2$ : pseudo-second-order model rate constant ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ),  $h_0$ : initial sorption rate for pseudo-second-order adsorption ( $\text{mg/g/min}$ ).

### 6.3 Avrami fractionary kinetic model

The exponential function of Avrami model was made to check specific changes of kinetic thermal parameters, original concentration, and adsorption time. Avrami model is expressed mathematically by Eq.16 (Bergmann and Machado, 2015; Inyinbor et al., 2016; Mohd et al., 2014).

$$q_t = q_e(1 - \exp(-K_{av} - t)^{nAV}) \quad \text{Eq.16}$$

Where,  $kAV$ : Adjusted kinetic constant ( $\text{min}^{-1}$ ),  $nAV$ : fractional adsorption order.

### 6.4 General order kinetic model

The model relies on the number of accessible sites on the surface of adsorbent. It is given in Eq. 17 (Bergmann and Machado, 2015):

$$q_t = q_e - \frac{q_e}{\left[ K_N(q_e)^{n-1} \cdot t \cdot (n-1) + 1 \right]^{1/1-n}} \quad \text{Eq.17}$$

with  $n \neq 1$ , Where:  $kN$ : kinetic adsorption rate constant ( $\text{min}^{-1} \cdot (\text{g/mg})^{n-1}$ ),  $n$ : order of adsorption.

### 6.5 Elovich model

Another rate equation called as Elovich model, in general applied successfully in chemical adsorption kinetics (McIntock, 1967). It assumes that the adsorption sites increase exponentially with adsorption followed by a slow rate diffusion. Which implies heterogeneous adsorbing surface (Zhang et al., 2017). It given in the mathematical Eq. 18.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \text{Eq.18}$$

The integration of equation 18 give as Eq. 19.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad \text{Eq.19}$$

Where,  $\alpha$ : initial adsorption rate ( $\text{mg/g} \cdot \text{min}^{-1}$ ),  $\beta$ : adsorption constant related to the surface coverage ( $\text{g/mg}$ ).

It is essential to studied precisely the kinetics adsorption to find best fit of two organic dyes on CAG, five kinetics models were tested by using nonlinear method as shown in figure 9. The determination of experimental kinetic adsorption parameters was recapitulated in Table 4. As referred in Table 4, the calculated adjacent R squared are closer to unity and the error functions values (SD, ) are smaller for avrami kinetic model than general kinetic order and pseudo-first order. Therefore with comparing the results of the five kinetics models the best

**Table 3.** Maximum dye removal capacity for Brilliant green and Erythrosine by some potential adsorbents.

Dye	Adsorbent	Maximum dye removal capacity (mg/g)	References
<b>Brilliant green</b>	Activated carbon prepared from acorn	2.1	(Ghaedi et al.,2011)
	Psidium guajava (Guava) leaves	1.075	(Rehman et al.,2015)
	peels of Solanum tuberosum (Potato)	1.173	(Rehman et al.,2015)
	Granular activated carbon (CAG)	5.405	Current study
<b>Erythrosine</b>	Pumpkin seed hulls	5.03	(Apostol et al .,2015)
	De-oiled mustard active carbon	3.46	(Jain et al.,2009)
	Cellulose granules	3,75	(Tabara et al.,2011)
	Granular activated carbon (CAG)	4.77	Current study

fit were obtained for Avrami kinetic model for erythrosine dye with  $R^2_{adj}$  equal to 0.9959. This is compatible with previous literature work like the sorption of Procion Red MX 3B onto brazilian pine fruit shell (Calvete *et al.*, 2009). Moving to the case of brilliant green, the modeling of adsorption kinetics is in accordance with the general order model ( $R^2_{adj}=0.9949$ ) at  $T=293K$  and it may also, support the second order kinetic and avrami model. Similar studies was reported on the adsorption process of tetracycline antibiotic on Zn-AC and methylene blue on canola residues (Takdastan *et al.*, 2016; Balarak *et al.*, 2015), therefore the adsorption capacity at equilibrium is very close to experimental values by the appropriate model for each dye.

### 7. Thermodynamic study

The constants of the Langmuir and Liu isotherms ( $K=K_g$  or  $K_L$ ) depend on temperature, consequently they can be used for estimating the thermodynamic quantities on adsorbed dyes by CAG, such as standard free energy change ( $\Delta G^\circ$ ), isosteric adsorption enthalpy ( $\Delta H^\circ$ ) and isosteric adsorption entropy( $\Delta S^\circ$ ) it was calculated as follows (Gopinathan *et al.*, 2016):

$$\Delta G^\circ = -RT \ln K \quad \text{Eq.20}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Eq.21}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Eq.22}$$

Where,  $K$  is the binding constant,  $R$  is universal gas constant ( $8,314J/mol/K$ ) and  $T$  is the experimental temperature ( $K$ ). When the  $\ln K$  is plotted versus the inverse of the temperature gives a straight line with the slope  $-\Delta H^\circ/R$ , and intercept  $\Delta S^\circ/R$ . The calculations results are given in Table 5. The Liu model showed the highest values of for both of dyes, which means that the values calculated of standard entropy and enthalpy, were reliable. In addition the positive and low  $\Delta H^\circ$  values shows that their interaction was an endothermic process of erythrosine and brilliant green adsorption on activated carbon. The negative  $\Delta G^\circ$  values indicated that the binding of erythrosine with activated carbon is a spontaneous physiosorption process ( $\Delta G^\circ < -20K J/mol$ ) (Balarak *et al.*, 2016), and the spontaneity increases with temperature. On the other hand, in the case of brilliant green the values of  $\Delta G^\circ$  is positive accompanied by decrease with increasing the temperature. Thus indicating an increase in thermodynamic feasibility at higher temperatures (Regti *et al.*, 2017), The calculations results are given in Table 5. The Liu model showed the highest values of for both of dyes, which means that the values calculated of standard entropy and enthalpy, were reliable. In addition the positive and low  $\Delta H^\circ$  values shows that their interaction was an endothermic process of erythrosine and brilliant green adsorption on activated carbon. The negative  $\Delta G^\circ$  values indicated that the binding

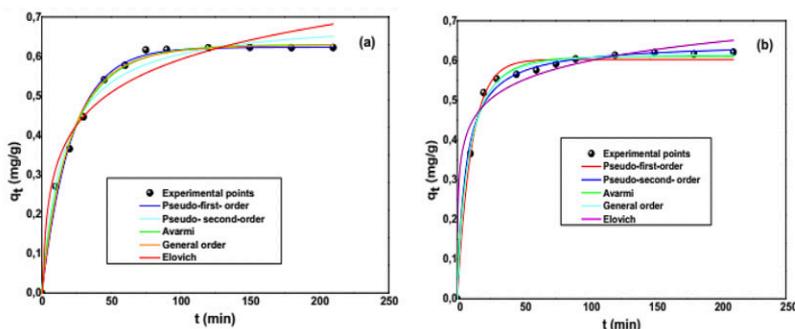


Figure 9. The curves of the five nonlinear modelled kinetics adsorption of Erythrosine (a) and Brilliant green (b) on activated carbon at  $T=293K$ .

**Table 4.** Experimental results of kinetic modeling of brilliant green and erythrosine on activated carbon.

Kinetic models and its parameters	Erythrosine	Brilliant green
qe(exp)	0.6218	0.61338
<b>Pseudo-first order</b>		
k <sub>1</sub>	0.0462	0.0922
q <sub>e</sub> (cal)	0.623	0.6026
RSS	0.0023	0.0027
X <sup>2 red</sup>	2.35x10 <sup>-4</sup>	2.72x10 <sup>-4</sup>
SD	0.0153	0.0173
R <sup>2</sup>	0.9943	0.9922
R <sup>2</sup> <sub>adj</sub>	0.9938	0.9914
<b>Pseudo-second order</b>		
k <sub>2</sub>	0.0924	0.2445
q <sub>e</sub> (cal)	0.6991	0.6454
h <sub>0</sub>	0.0451	0.1018
RSS	0.00519	0.0023
X <sup>2 red</sup>	5.18x10 <sup>-4</sup>	2.99 x10 <sup>-4</sup>
SD	0.0227	0.0173
R <sup>2</sup>	0.9875	0.9934
R <sup>2</sup> <sub>adj</sub>	0.9863	0.9927
<b>Elovich</b>		
α	0.1634	3.688
β	8.2859	14.3108
RSS	0.0177	0.00102
X <sup>2 red</sup>	0.0017	0.00103
SD	0.0421	0.032
R <sup>2</sup>	0.9574	0.9707
R <sup>2</sup> <sub>adj</sub>	0.9532	0.9678
<b>General order</b>		
qe(cal)	0.6298	0.6173
k <sub>n</sub>	0.0533	0.1482
n	1.1469	1.4488
RSS	0.001	0.0014
X <sup>2</sup>	2.26 x10 <sup>-4</sup>	1.62 x10 <sup>-4</sup>
SD	0.015	0.0127
R <sup>2</sup>	0.9951	0.9958
R <sup>2</sup> <sub>adj</sub>	0.994	0.9949
<b>Avrami</b>		
q <sub>e</sub> (cal)	0.6298	0.6103
k <sub>AV</sub>	0.046	0.0969
n <sub>AV</sub>	0.8764	0.7561
RSS	0.0014	0.002
X <sup>2 red</sup>	1.65 x10 <sup>-4</sup>	2.31 x10 <sup>-4</sup>
SD	0.0127	0.0152
R <sup>2</sup>	0.9964	0.994
R <sup>2</sup> <sub>adj</sub>	0.9956	0.9927

**Table 5.** Thermodynamic parameters of dyes adsorption onto activated carbon.

T(K)	Erythrosine						Brilliant green					
	293	298	303	293	298	303	293	298	303	293	298	303
Isotherm	Langmuir			Liu			Langmuir			Liu		
$\Delta S^0$ (J/K/mol)	141.581			143.263			257.607			175.526		
$\Delta H^0$ (KJ/mol)	41.428			41.459			80.409			54.955		
$\Delta G^0$ (KJ/mol)	-0.19	-0.47	-1.62	-0.55	-1.16	-1.98	4.78	3.94	2.19	3.49	2.73	1.72

of erythrosine with activated carbon is a spontaneous physiosorption process ( $\Delta G^0 < -20$  K J/mol) (Balarak *et al.*, 2016), and the spontaneity increases with temperature. On the other hand, in the case of brilliant green the values of  $\Delta G^0$  is positive accompanied by decrease with increasing the temperature. Thus indicating an increase in thermodynamic feasibility at higher temperatures (Regti *et al.*, 2017).

## 8. Conclusions

This study dealt with the application of activated carbon as an effective sorbent for rapid removal of two organic dyes in aqueous solution. Different parameters related to the operating conditions (initial concentration of dye, pH, stirring speed, and temperature) were estimated by batch tests. For all kinetic data the adsorption mechanism provided the best correlation by a kinetic of the Avrami model in case of erythrosine with  $R^2_{adj} = 0.9956$  and general order in case of brilliant green with  $R^2_{adj} = 0.9949$ . The plot of experimental adsorption isotherm data for both dyes favorably followed the Liu isotherm model. The obtained results of thermodynamic effect proved that the adsorption of the erythrosine dye is endothermic and spontaneous process in nature and non-spontaneous for the brilliant green dye within the limits of physical adsorption.

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- K Binding constant  
 $k_{AV}$  Avrami kinetic constant  
 $K_F$  Freundlich isotherm constant  
 $K_g$  Equilibrium constant of Liu isotherm  
 $K_L$  Equilibrium constant of Langmuir isotherm  
 $k_N$  kinetic adsorption rate constant  
m Mass  
N Total number of experimental data  
n Order of adsorption  
 $n_{AV}$  Avrami fractional adsorption order  
 $n_F$  Adsorption intensity  
 $n_L$  Dimensionless exponent of the Liu equation  
P Number of parameters of the fitted model  
pH Potential of hydrogen  
Pr Pressure  
 $q_e$  Adsorbed amount at equilibrium  
 $q_m$  maximum adsorption capacity  
 $q_t$  Adsorbed amount at time t  
R universal gas constant  
 $R^2$  Coefficient of determination  
RSS Residual sum squares  
 $R^2_{adj}$  Adjusted R-squared  
SD Standard deviation  
SEM Scanning electron microscope  
T Temperature  
t Time  
V Volume  
v Agitation speed  
 $V_{ads}$  Adsorbed volume  
Reduced Chi-squared  
 $\lambda_{max}$  Wavelength of maximum absorbance  
 $\alpha$  Initial adsorption rate  
 $\beta$  Adsorption constant related to the surface coverage  
 $\Delta H^0$  Adsorption enthalpy  
 $\Delta G^0$  Free energy of adsorption  
 $\Delta S^0$  Adsorption entropy

## Abbreviations

- A° Angstrom  
CAG Granular activated carbon  
 $C^0$  Initial concentration  
 $C_e$  Residual concentration at equilibrium  
 $C_t$  residual concentration at time t  
Eq Equation  
 $h^0$  Initial sorption rate for pseudo-second-order adsorption  
 $k_1$  Pseudo-first-order adsorption rate constant  
 $k_2$  Pseudo-second-order adsorption rate constant