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Kinetics and Modeling of the adsorption of methylene blue by the grafted cotton.

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Abstract: The cotton grafted by succinic anhydride (AS) is used for the remove of methylene blue (M.B) from aqueous solution. Studies concerning the sorption kinetics (i.e. the effects of contact time, dye concentration) are discussed. A large adsorption capacity is observed: the order of 714 mg/g support grafted. In the present work we tested four equations insulated (Langmuir, Freundlich, Temkin and Generalized), and we have determined the characteristic parameters for each isotherm. The experimental results allow us to suggest the use of cotton registry by the succinic anhydride as adsorbent for the treatment of industrial waters.

Keywords: Adsorption; cellulose, desorption, dyes removal, grafting, textile wastewater

INTRODUCTION

The textile industry is responsible to produce a large volume of polluted effluents discharging to the receiving environment. The presence of dyes in effluents cause many damage to the ecological system of the receiving surface water [1-2] and create a lot of disturbance to the groundwater resources. In order to minimise the risk of pollution problems from such effluents, it is necessary to accurately treat them before discharging to the environment. Substantial attempts have been made by many researchers to find suitable treatment systems in order to treat wastes discharged from different industries in particular textile industry[1-4].

A wide range of chemical and physical procedures of dyes removal from aqueous solutions are based on the decolourization by photocatalytic degradation[4-6] membranes[7], microbiological decomposition[8]

electrochemical oxidation of dye[9] and adsorption techniques[10-15]. From all these techniques for dye removal from industrial effluents, the adsorption process is noted to be superior because it is economically cost effective, efficient[11] and simple [12].

In the present study, the cotton grafted by succinic anhydride is used to remove methylene blue (M.B) dye from the aqueous solution. Different equilibrium data are processed by a plurality of adsorption isotherm (Langmuir, Freundlich, Temkin and Generalization) to choose an appropriate model isotherm. A kinetics study of the adsorption process is also considered in the present study to suggest the use of cellulosic material.

MATERIALS AND METHODS

Sorbent: The material used in this work is the grafted cotton with carboxyl groups using succinic anhydride (SA). The chemical modification of cotton was carried out successfully with a grafting rate[16] equal to 140%.

Adsorbate: The sorption capacity was investigated using Methylene blue (M.B) as model molecule for basic dyes. This dye was commercial product and used without purification. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water to give a concentration of 1000mg/L and diluting when necessary (see **Figure 1** for the structural formulae) [17].

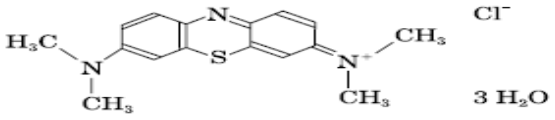


Fig. 1: Chemical structure of Methylene blue (M.B) (λmax: 664 nm).

Batch adsorption experiments: Adsorption experiments were carried out by shaking 0.1 g of cotton grafted with 20mL of dye solution for the desired dye concentration and pH. Studies were conducted at 25 ◦C. Methylene blue residual concentration was estimated using the spectrophotometric technique at the wavelength of 664 nm. The samples were taken from the shaker at predetermined time intervals for kinetics and at equilibrium time for isotherms. To calculate the dye removal capacity at equilibrium time (Qe) or the removal efficiency, will be determined respectively according to the following equations:

$$Qe = [(C_0 - Ce) \times V/M] \quad (mg/g) \qquad (1)$$

$$\text{Removal efficiency} = (C_0 - Ce) \times 100/C_0 \quad (\%) \qquad (2)$$

Where Co is the initial dye concentration in liquid phase (mg/ L); Ce is the liquid phase dye concentration at equilibrium (mg/ L); V is the volume of dye solution used (L); and m is the mass of sorbent used (g).

RESULTS AND DISCUSSION

The adsorption properties and equilibrium data, known as adsorption isotherms, describes how contaminants interact with absorbent materials and are therefore critical in optimizing the use of adsorbents. To optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve[18, 19].

Adsorption of Methylene Blue by grafted cotton: To compare the performance of adsorption of dyes on cotton grafted, no grafted, and cotton treated with NaOH and $KMnO_4$, we made preliminary tests of adsorption in batch system on different samples under the same conditions. The results obtained are summarized in **Figure 2.**

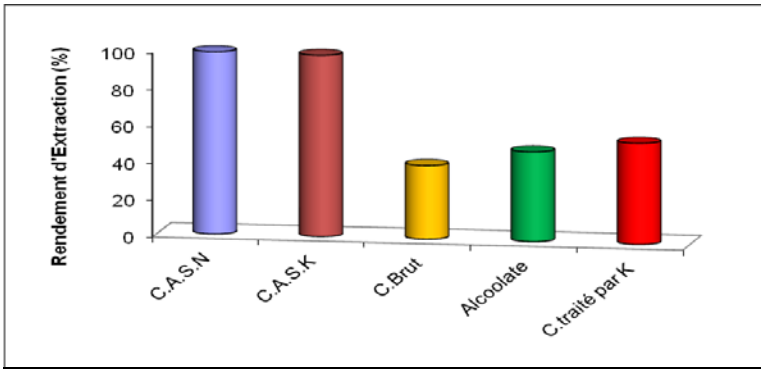


Fig.2: Comparison between adsorption capacities (R in %) of M.B on different materials. (Contact time = 2 h; temperature = 25 °C; pH = 10).

The adsorption capacity was expressed as rate of absorption (R %) which represents the ratio between the amount of dye adsorbed and the initial quantity of dye. The experiments were performed under identical conditions. As shown in **Figure 2,** the results obtained with the adsorbent (ASK and ASN) shows the maximum extraction of M.B. The presence of carboxyl groups in the material significantly increases the sorption properties: it shows that these groups contribute to the mechanism of sorption by electrostatic interactions between the COO- groups of the material and the reactive group of M.B [20].

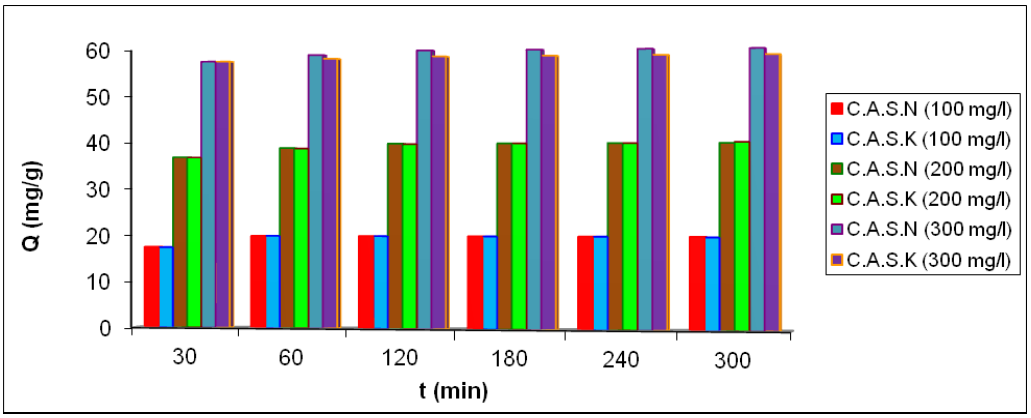


Fig.3: Kinetics of adsorption capacity of M.B by C.A.S at three different concentrations (Temperature = 25°C; pH=10).

Figure 3 shows the amount of adsorbed M.B (mg to 1 g) as a function of contact time at three different concentrations of the dye solution. The amount of dye adsorbed increases with the contact time and reached equilibrium after 60 min for three concentrations. In addition, Q increases with the

Concentration of M.B increases and it can be explained by the strong chemical interactions between the M.B and the carboxylic groups. To find the order of the adsorption kinetics of M.B, the first order

kinetic equation has been tested, the graphs Q / t versus t were plotted (Fig. 4). The sorption kinetics can be described by a second model. The differential equation is as follows[21]:

$$dQt / dt = K1 (Qe - Qt)^2 \qquad (3)$$

Where Qe is the amount of dye adsorbed at equilibrium (mg g^{-1}); Qt is the amount of dye adsorbed at time t (mg g^{-1}); and k is the equilibrium rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). Integrating Eq. (3) for the boundary conditions t = 0 to t = t and Qt = 0 to Qt = Qt gives:

$$\frac{1}{(Q_e - Qt)} = \frac{1}{Q_e} + kt \qquad (4)$$

Which is the integrated rate law for a pseudo-second order reaction? Eq. (4) can be rearranged to obtain a linear form:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q^2_e} + \frac{t}{Q_e} \qquad (5)$$

And:

$$\mathbf{h = k\, Q^2_e}$$

Where h is the initial rate of sorption (mg g^{-1} min^{-1}). The rate parameters k and Q_e can be obtained directly from the intersection and the slope of the plot of t / Q_t against t. Figure 4 shows the pseudo-first order kinetics of the second adsorption M.B onto adsorbent at three different concentrations. The values of k and Q calculated from figure 4 are summarized in Table 1. It is clear that the kinetics of M.B adsorption onto material follows this model, with regression coefficients greater than 0.990 for the three concentration used in this study. In addition, the adsorption capacity, Qe, increases with increasing concentration, which is also shown in figure 4.

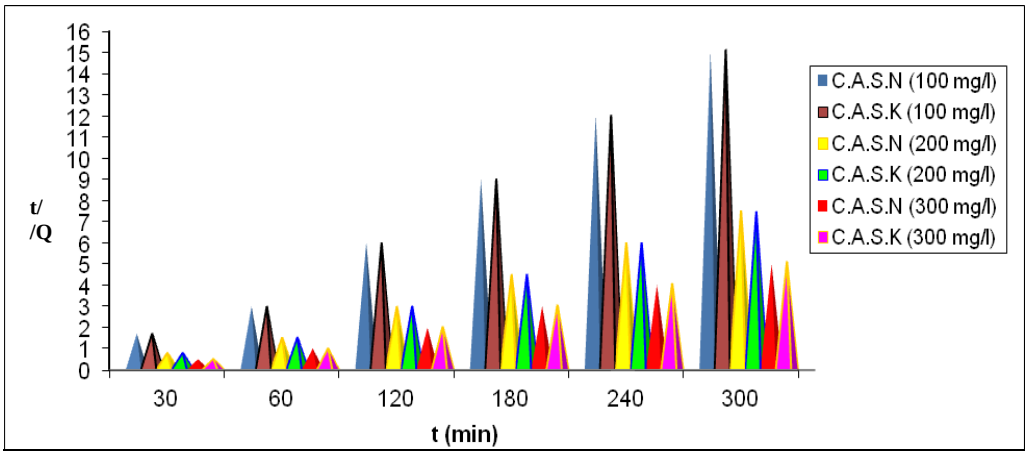


Fig. 4: Pseudo-second order kinetics of M.B adsorption onto C.A.S at three different Concentration (temperature = 25 °C; pH = 10).

Table 1: Kinetics parameters for M.B adsorption onto C.A.S with different concentrations (Temperature = 25 °C; pH = 8).

Concentration (mg)	K ($mg\ g^{-1}\ min^{-1}$)	Q_e (mg/g)	R^2
100	**0.886**	**19.96**	**0.9989**
200	**0.672**	**40.16**	**0.9993**
300	**3.976**	**58.48**	**0.9999**

The calculated values agree very well with experimental data, indicating that the sorption system studied belongs to the second order kinetic model.

Equilibrium studies: An adsorption isotherm represents the relationship existing between the amount of pollutant adsorbed and the pollutant concentration remaining in solution.

Adsorption equilibrium is established when the amount of pollutant being adsorbed onto the material is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phaseconcentration graphically it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to sorption equilibrium[22,23].

The influence of the dye concentration on adsorption capacity: Figure 5 shows the adsorption equilibrium of M.B (Qe against Ce) using the grafted cotton. The isotherm rises sharply in the early stages with low values of Ce and Qe, indicating that there are many easily accessible sites. The adsorbent is saturated when the plateau is reached.

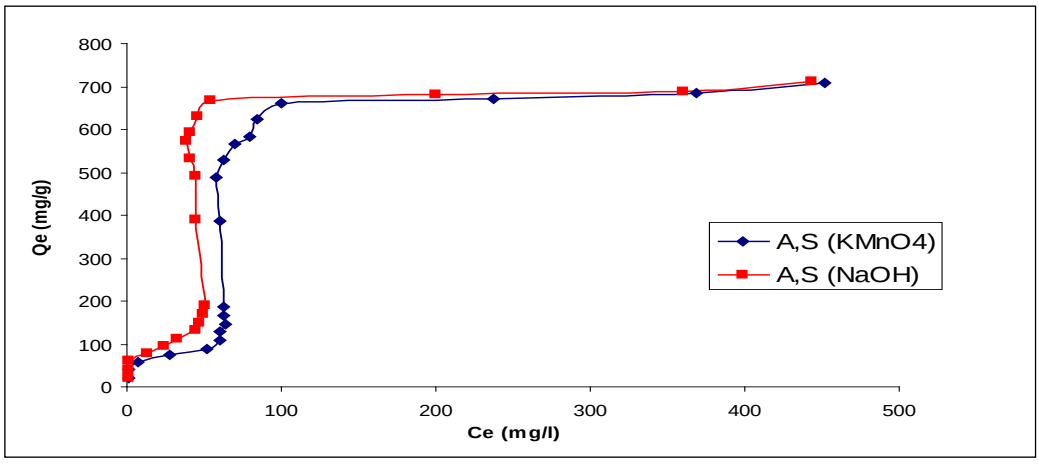


Fig. 5: Adsorption isotherm for M.B by C.A.S (contact time = 2 h; sorbent = 100 mg; Temperature = 25°C; pH = 8).

There are several isotherm equations available for analyzing experimental data of sorption equilibrium, including Freundlich, Langmuir, Temkin, and Generalized. However, the two most common types of isotherms are Langmuir and Freundlich. Four isotherm equations were tested in this work, namely Langmuir, Freundlich, Temkin and generalized.

The Langmuir isotherm: The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogeneous sites within the adsorbent[22, 25.]

The application of the Langmuir model suggests that the sorptional energy is constant and does not depends on the degree of occupation of the active centres of an adsorbent. It also assumes that once a dye occupies a site, no further sorption can take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighbouring sites. The linearized equation of Langmuir is represented as follows:

$$Q_e = \frac{x}{m} = \frac{K_L.C_e}{1 + a_L.C_e} \qquad (6)$$

Where x is the amount of dye adsorbed (mg); m is the amount of adsorbent used (g); C_e (mg L^{-1}) and Qe (mg g^{-1}) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; K_L (L g^{-1}) and a_L (Lmg^{-1}) are the Langmuir isotherm constants.
The Langmuir isotherm constants, K_L and a_L are evaluated through linearization of Eq. (7):

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (7)$$

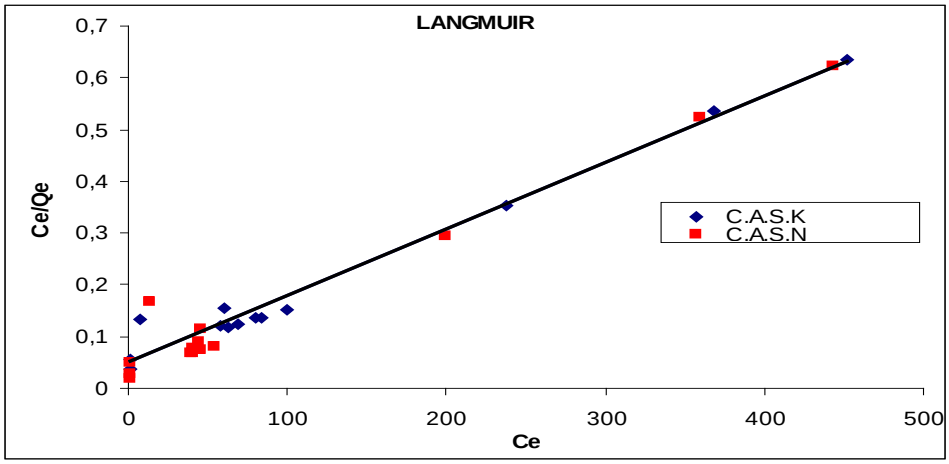
Hence by plotting C_e/Q_e against C_e it is possible to obtain the value of K_L from the intercept which is $1/K_L$ and the value of a_L from the slope, which is a_L/K_L. The theoretical monolayer capacity is Q_o (or Q_{max} the maximum adsorption capacity of the adsorbent) and is numerically equal to K_L/a_L.

The Langmuir equation is applicable to homogeneous sorption, where the sorption of each molecule onto the surface has equal sorption activation energy. The equation is thermodynamically consistent and follows Henry's Law at low concentrations. As Ce becomes lower, a_LC_e is much less than unity and Qe = K_LC_e, that is analogous to Henry's law. Alternatively, at high adsorbate concentrations, the model predicts a constant monolayer adsorption capacity[22].

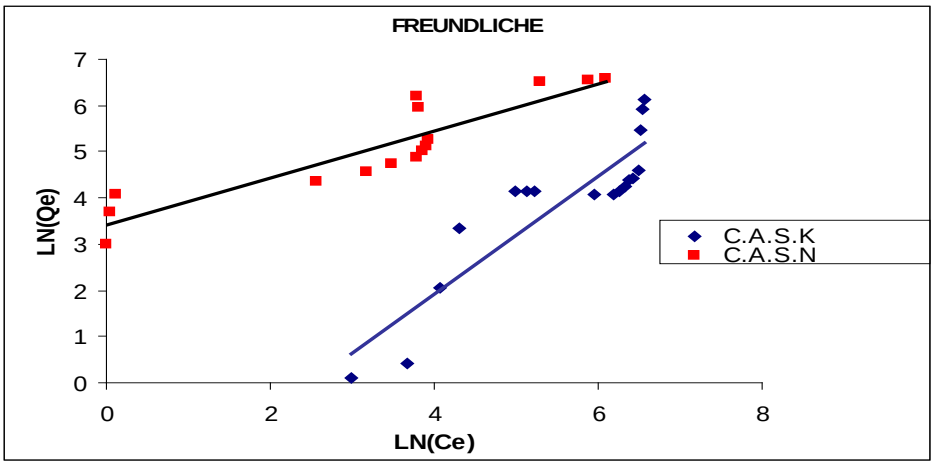
The plot of equilibrium concentrations of M.B in the solid and liquid phases that is C_e/Q versus C_e is presented in Figure 6(a). From this plot, the Langmuir constants were found to be: Q_{max} = 714.285mg g^{-1}; K_L = 0.048 L g^{-1} with R^2=0.995.

The value of the monolayer saturation capacity demonstrates that the C.A.S exhibits interesting sorption properties toward cationic dyes.

The fit is well for the adsorption system under the concentration range studied (correlation coefficient, R^2= 0.995). The value of R^2 is higher than the other three isotherm values. Apparently, the plots in **Fig. 6** demonstrate that the Langmuir equation provides a reasonable description of the experimental data.


LANGMUIR
Ce/Qe
Ce
C.A.S.K
C.A.S.N
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
100
200
300
400
500

(a)


FREUNDLICHE
LN(Qe)
LN(Ce)
C.A.S.K
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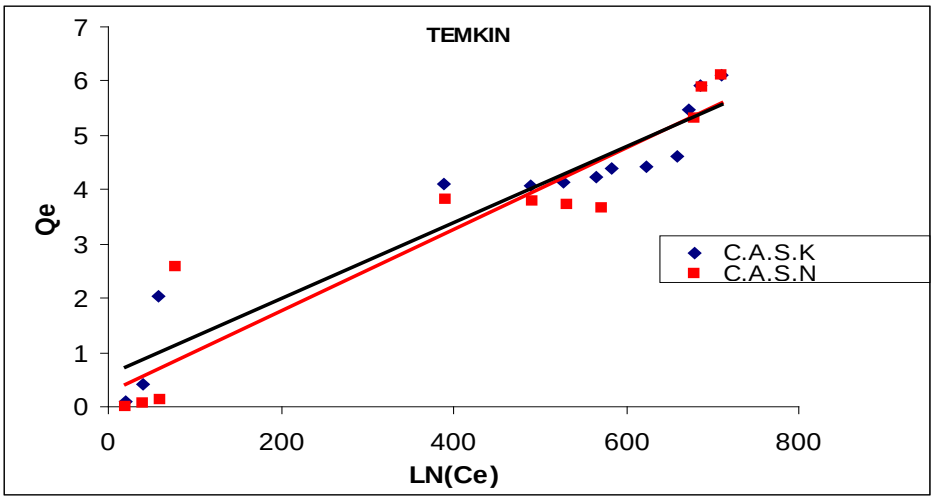
(b)


TEMKIN
Qe
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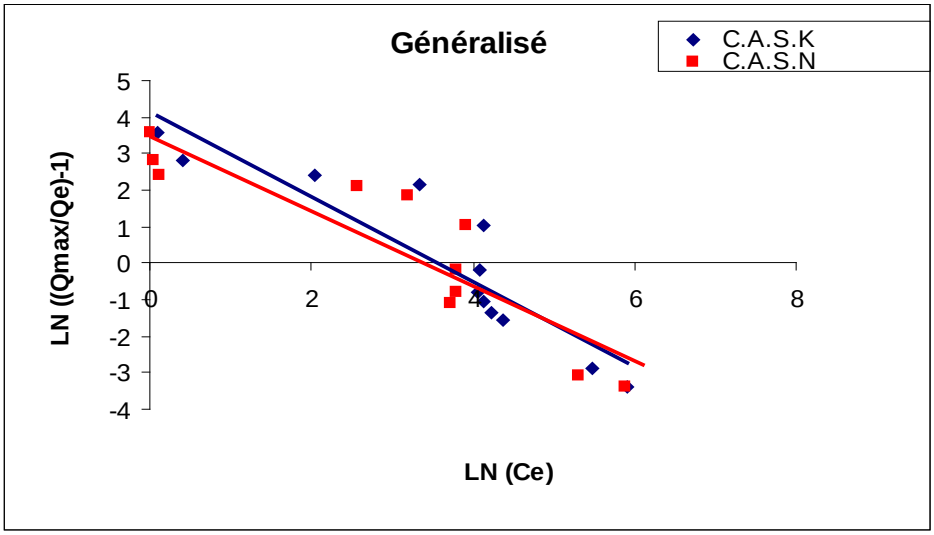

(d)

Fig. 6: Adsorption isotherms for M.B by C.A.S (a) Langmuir isotherm; (b) Freundlich isotherm; (c) Temkin isotherm and (d) generalized isotherm.

3.2.3. The Freundlich isotherm: The Freundlich isotherm is the earliest known relationship describing the sorption equation[26.] The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centres of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation[22, 26]:

$$Q_e = K_F . C_e^{1/n_F} \qquad (8)$$

Where Q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_F is Freundlich constant (L g^{-1}), and $1/n_F$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n_F are empirical constants dependent on several environmental factors. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (8):

$$LnQ_e = LnK_F + \frac{1}{n_F} LnC_e \qquad (9)$$

Therefore, the plot of ln Q_e versus ln C_e was employed to generate the intercept value of K_f and the slope of $1/n_F$. The results are given in Fig. 6(b) and Table 2.

However, equilibrium adsorption data of M.B did not fit to the Freundlich isotherm well. The value of R^2 (R^2= 0.887) is much lower than the Langmuir isotherm value.

The Langmuir model yields a much better fit than the Freundlich model.

Table 2: Summary of the isotherm constants and the correlation coefficients for different isotherms

Supports	Langmuir Isotherm				Freundlich Isotherm		
	K_L (L/g)	Q_{max} (mg/g)	R^2	r	n	K_F (L/g)	R^2
C.A.S.N (B.M)	0.048	714.285	0.995	0.171	1.624	19.307	0.887
C.A.S.K (B.M)	0.033	769.230	0.994	0.232	1.624	19.307	0.809
	Temkin Isotherme			**Generalized Isotherm**			
	A (L/G)	**B**	R^2	**K (mg/L)**	**n**	R^2	
C.A.S.N (B.M)	0.328	124.523	0.889	6.354	1.159	0.832	
C.A.S.K (B.M)	0.708	113.427	0.912	3.303	1.028	0.806	

3.2.4. The Temkin isotherm: The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centres of an adsorbent is increased. This model takes into account the presence of indirect adsorbate/adsor-bate interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage.
The Temkin isotherm has been used in the following form[22,27]:

$$Q_e = \frac{RT}{b} LnAC_e \qquad (10)$$

A linear form of Eq. (10) can be expressed as:

$$Q_e = \frac{RT}{b} LnA + \frac{RT}{b} LnC_e \qquad (11)$$

Where RT/b = B and A are the Temkin isotherm constants. The constant B is related to the heat of adsorption. Ignoring very low and very large values of concentration, the adsorption data can be analyzed according to the Temkin equation (Eq. (12)):

$$Q_e = BLnA + BLnC_e \qquad (12)$$

A plot of Qe versus ln Ce enables one to determine the constants A and B.
The values of the Temkin constants and the correlation coefficient are listed in Table 2. The correlation coefficient is lower than and Freundlich values. From the Fig. 6(c), it is also clear that the Langmuir model yields a much better fit than the Temkin model.

3.2.5. Generalized isotherm: The generalized adsorption isotherm has been used in the following form[28]:

$$Q_e = Q_{\max} \frac{C_e^n}{K + C_e^n} \qquad (13)$$

A linear form of this equation is:

$$Ln\left(\frac{Q_{\max}}{Q_e} - 1\right) = LnK - n\ LnC_e \qquad (14)$$

Where K is the saturation constant (mg L-1); n is the cooperative binding constant; Qmax is the maximum adsorption capacity of the adsorbent (mg g-1); Q (mg g-1) and Ce (mg L-1) are the equilibrium dye concentrations in the solid and liquid phase, respectively A plot of the equilibrium data in form of ln[(Qmax/Qe)-1 versus ln Ce gives K and n constants. The following values were found for the constants of the generalized adsorption isotherm K=6.354 mgL-1, n= 1.159 with R2=0.832. The value of correlation coefficient is much lower than the other three isotherm values.
The generalized equation represents the poorest fit of experimental data than the other isotherm equations.

4. CONCLUSIONS

Equilibrium and kinetic studies were made for the adsorption of methylene bleu (M.B) from aqueous solutions onto cotton grafted. Results of adsorption showed that the support can be effectively used as an adsorbent for the removal of cationic dye. These adsorbents exhibited high sorption capacities toward M.B: the monolayer adsorption capacity was 714.285 mg g-1. The adsorption capacity increased as the concentration of the material increased. However, the sorption was dependent on the presence of carboxylic groups. The straight lines in plot of t/Qt versus t showed good agreement of experimental data with the second order kinetic model for different initial sorbent concentration. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and generalized isotherms and the characteristic parameters for each isotherm have been determined. The results showed that the experimental data were correlated reasonably well by the Langmuir adsorption isotherm.

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