

CATIONIC DYE REMOVAL BY SUGARCANE BAGASSE ACTIVATED CARBON FROM AQUEOUS SOLUTION

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ABSTRACT

Low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated wastewater. Sugarcane Bagasse, an abundant agriculture waste in Egypt, was used in the present study to prepare activated carbon. Batch adsorption experiments were conducted to study its effectiveness to remove cationic dye methylene blue from aqueous solution. The effects of initial dye concentrations, agitation time, solution pH and temperature on methylene blue dye removal were investigated. The optimum pH value for the maximum percentage removal of the dye was 7. Adsorption isotherms were determined and modeled with Redlich–Peterson, Langmuir and Freundlich equations at 20 °C. The kinetic data were analyzed using Pseudo-first order, pseudo-second order. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°) and free energy (ΔG°) were determined. The equilibrium data were best fitted to the Redlich–Peterson isotherm model. The adsorption kinetics was found to follow the pseudo-second-order kinetic model with good correlation coefficient. The positive ΔH° value indicated that the adsorption process was endothermic in nature. The results revealed sugarcane bagasse activated carbon could be employed as a low-cost alternative adsorbent in wastewater treatment.

Keywords: Activated carbon, Methylene blue, Adsorption, Isotherm, Kinetics

1. Introduction

Dyes are considered to be particularly dangerous organic compounds for the environment and public health. Industries such as textile, leather, paper, plastics are sources for dye effluents. Discharging these effluents in water bodies reduces light penetration, affects photosynthesis of aqueous flora and may disturb the ecosystem (Hajati *et al.*, 2014). Dyes can cause a severe health hazard to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous system, they can cause allergy, dermatitis, skin irritation (Brookstein *et al.*, 2009) and may be mutagenic and carcinogenic to humans (De Lima *et al.*, 2007). Methylene blue dye (MB), a cationic basic dye, is mainly used for dyeing cotton and silk (Deng *et al.*, 2011). It can cause vomiting, nausea, hypertension and methemoglobinemia (Foo, 2012). Therefore, treatment of dyes from process effluent before discharging into receiving waters becomes environmentally important and of public health concerns.

Various techniques have been employed for the removal of dyes from wastewaters. Adsorption was the superior to other techniques due to its flexibility, simplicity of design and ease of operation (Rafatullaha *et al.*, 2010; Demiral *et al.*, 2011; Vučurović *et al.*, 2014). Adsorption by activated carbon is one of the most widely used techniques and is considered to be an effective method for the removal of dyes from wastewater. Activated carbons have high porosity and high surface area for adsorption (Spahisa *et al.*, 2008). In addition; the chemical nature of their surfaces enhances adsorption. However, its use is limited due to its high-cost. Several studies investigated the development of activated carbon from cheap and available materials. Agricultural by-products used for the preparation of activated carbon have minimum cost moreover the benefits of the preparation of activated carbon from agricultural by-products would also include removal of polluting waste product and economic gains for products manufactured from abundant sources (Ghaedi *et al.*, 2014). Agricultural by-products and waste materials used for the production of activated carbons include, apricot stones (Djilani *et al.*, 2015) olive stone (Hazzaa and Hussein, 2015), pomegranate peel (Amin, 2009), bamboo (Hameed *et al.*, 2007), coconut husk (Foo and Hameed, 2012), pistachio shell (Dolas *et al.* 2011), rambutan peel (Ahmad and Alrozi, 2011), walnut shells (Yang and Qiu, 2010) , and sugarcane bagasse (Silva *et al.*, 2011)

In Egypt, sugarcane bagasse is abundantly available agricultural wastes and can be an adequate raw material to obtain good active carbon. In this study, activated carbon was prepared from sugarcane bagasse by thermal activation in absence of air. The aim of that study was to investigate the adsorptive removal of MB dye onto activated carbon prepared from sugarcane bagasse. Effective parameters such as pH, initial dye concentration, agitation time, and temperature were investigated. The equilibrium and kinetic data of the adsorption were then studied. The adsorption mechanisms were investigated and thermodynamic parameters were also determined.

2. Materials and methods

2.1 Adsorbate

Cationic basic dye, methylene blue (MB) purchased from Merck was chosen as the adsorbate in this study, and was not purified prior to use. The stock solution was prepared by dissolving 1 g of dye in one litre double distilled water. All chemicals used, were of analytical reagent grade. The chemical formula of methylene blue dye is $C_{16}H_{18}N_3ClS$ and its molecular weight is 319.85. The pH of initial dye solution can be adjusted by the addition of dropwise of 0.1 N HCl or 0.1 N NaOH and measured using a pH meter. All chemicals used were of analytical reagent grade.

2.2 Preparation of activated carbon

Sugarcane bagasse used in the present study for production of activated carbon was collected from local markets, Egypt. It was washed thoroughly with double distilled water to remove any dust and impurities, oven dried at 105 °C for 4 hours, crushed, and sieved to a particle size of 0.42–0.85 mm in diameter using standard sieves (Model $\Phi 200$). Activated carbon was prepared according to our previous study (Hazzaa and Hussein 2015). Briefly the dried sugarcane bagasse was subjected to thermal activation by carbonization in a muffle furnace. The sample was placed in a 315 stainless steel covered tube in the muffle furnace, where it was physically activated and carbonized in the absence of air at different carbonization temperatures (500–900 °C) and at times (30–120 min). At the end of activation time, the carbonized samples were withdrawn from the furnace, allowed to cool and stored in tightly closed bottles. The most efficient carbonization temperature was achieved at 800 °C and activation time 60 min.

Scanning electron microscope (SEM) analysis was performed to study the morphology of SBAC (model SEM JEOL JSM 6360 LA Japan).

2.3 Adsorption studies

Batch adsorption studies were conducted in a set of 250 ml Erlenmeyer flasks containing 1 g adsorbent dose of particle size (0.42 - 0.85 mm) and 100 ml dye solutions with various initial concentrations. The

flasks were agitated in an isothermal water-bath shaker at 150 rpm and 20 ± 1 °C. The samples were taken at different time intervals until the equilibrium was reached. The experimental data were analysed for equilibrium and kinetic studies. The effects of initial concentration of MB (10, 30, 50, 70 and 100 mg l⁻¹), agitation time (5-120 min), pH of the solution (2–9) and the temperature (20, 30, 40 and 50 °C) on the adsorptive removal of MB were investigated. The samples withdrawn were centrifuged for 10 min and 1000 rpm. The dye concentration before and after adsorption were determined using UV–vis spectrophotometer (Shimadzu UV-1601, Japan) at wavelength 660 nm. All experiments were performed in duplicates. MB uptake at time t , q_t (m $g g^{-1}$), and at equilibrium, q_e (m $g g^{-1}$), was calculated by the following equation:

$$q_t = \frac{(C_i - C_t)}{W} \times V \quad (1)$$

$$q_e = \frac{(C_i - C_e)}{W} \times V \quad (2)$$

where C_i , C_e and C_t (mg l⁻¹) are the initial, equilibrium concentrations, and concentration at time t of dye, respectively, V (l) is the volume of the solution, and W (g) is the mass of adsorbent used

The percentage removal of MB was calculated as follows:

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

3. Results and discussion

3.1 Scanning electron microscopy

Figure 1 shows SEM micrograph of the SBAC with different magnification power. The carbonization of sugarcane created pores and holes. The produced activated carbon presented a uniform porous structure. The surfaces of the thermally carbonized carbons are full of cavities indicating the possibility for the dye to be adsorbed.

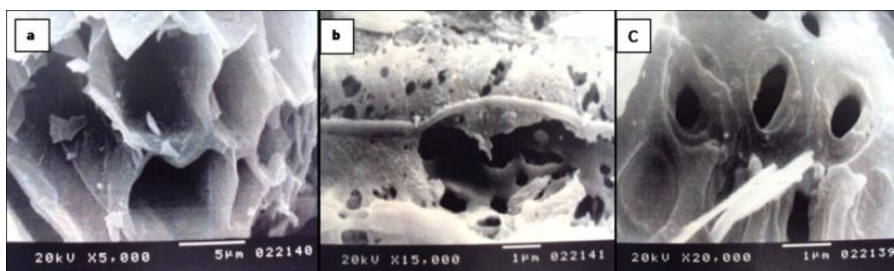


Figure 1. Scanning electron micrographs (SEM) of SBAC (a) magnification 5000, (b) magnification 15000, (c) magnification 20000

3.2. Batch adsorption experiments

3.2.1. Effect of initial concentration of dye and agitation time on adsorption

The effect of agitation time and initial concentration of MB in the solution on adsorption onto the SBAC was studied and shown in Figure 2. The experiments were carried out at adsorbent dose 1 g/100 ml, temperature 20 °C, pH 7 and at different initial concentrations of MB (10, 30, 50, 70 and 100 mg l⁻¹) for different time intervals. The results showed that the MB removal was fast at the initial stages of the contact time, and slowed down near equilibrium. Fig. 2 showed rapid removals of dye in the first 20 min which indicates a high degree of affinity of the interacting groups on the surface of the activated carbon.

The contact time needed for MB solutions with initial concentrations of 10 mg l⁻¹ to reach equilibrium was less than 60 min. However, for MB solutions with initial concentrations 100 mg l⁻¹ longer equilibrium times were reached at 120 min. The results revealed that the percentage removal of dye decreased with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface (Salleh *et al.*, 2011). The percentage removal of MB adsorbed decreased from 88% to 55% as the initial concentration increased from 10 to 100 mg l⁻¹. A large number of vacant surface sites were available for adsorption during the initial stage, and after a period of time, the remaining vacant surface sites were occupied. At low concentrations there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will not be available. Similar results were reported in previous studies (Hameed *et al.*, 2007; El Nemr *et al.*, 2009).

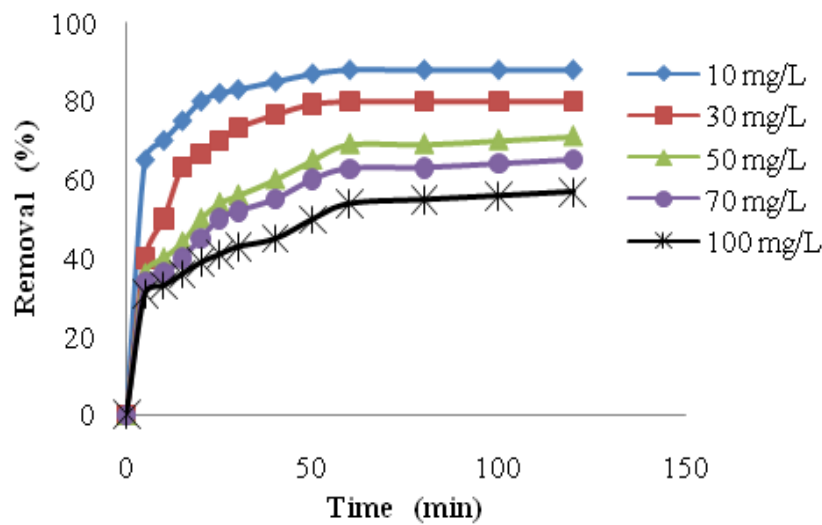


Figure 2. Effect of agitation time on adsorption of MB at various initial concentrations (Temperature =20 °C, pH= 7, SBAC dose =10gL⁻¹, agitation speed = 150 rpm).

3.3.2. Effect of solution pH on adsorption

The pH factor is an important factor in the adsorption process can significantly influence adsorption of dyes. The effect of solution pH on MB removal by SBAC in pH range of 2–9 with initial MB concentration of 100 mg l⁻¹, SBAC dosage of 1 g/100 ml and adsorption temperature of 20 °C was shown in Figure 3.

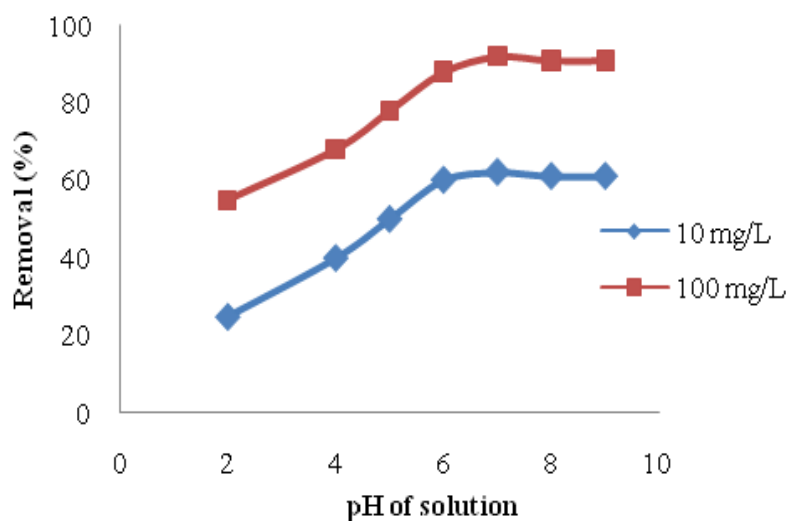


Figure 3. Effect of solution pH on MB adsorbed by SBAC

It can be seen that the dye removal efficiencies by SBAC increase with increasing pH. At pH 2 the percentage removal of dye was 25% and 55% for initial concentration 10 mg l⁻¹ and 100 mg l⁻¹ respectively, while, at pH 7 the percentage removal of dye was 62% and 90% for initial concentration 100 mg l⁻¹ and 10mgL⁻¹ respectively. Similar observations were previously reported (El-Sayed, 2011). The percentage removal MB dye on the SBAC was minimum at lower pH may be due to the competing proton ions with the cationic MB dye for the adsorption on the SBAC. However, at higher solution pH, the number of negatively charged surface sites on the adsorbent increased which may increase the electrostatic attractions between the positively charged dye cations and negatively charged adsorption sites, thus increased the removal of dye (Al-Degs, 2008).

3.4.3 Effect of temperature on adsorption

The effect of solution temperature on the adsorption process was studied by varying the adsorption temperature at 20, 30, 40 and 50 °C, adsorbent dose 1gm and initial dye concentration of MB 10 mg l⁻¹ and 100 mg l⁻¹ of MB. Figure 4 shows that increasing the temperature from 20 - 50 °C; increase the percentage removal from 60% to 85% respectively for initial concentration of MB 100 mg l⁻¹. However for initial concentration of MB 10 mg l⁻¹ the percentage removal increased from 92% to 99% for the increase of temperature from 20-50 °C respectively. Increasing temperature may decrease the viscosity of the solution and increase the rate of diffusion of the dye to the external boundary layer and the internal pores of the activated carbon. Similar results were also reported. (Gürses *et al.*, 2014).

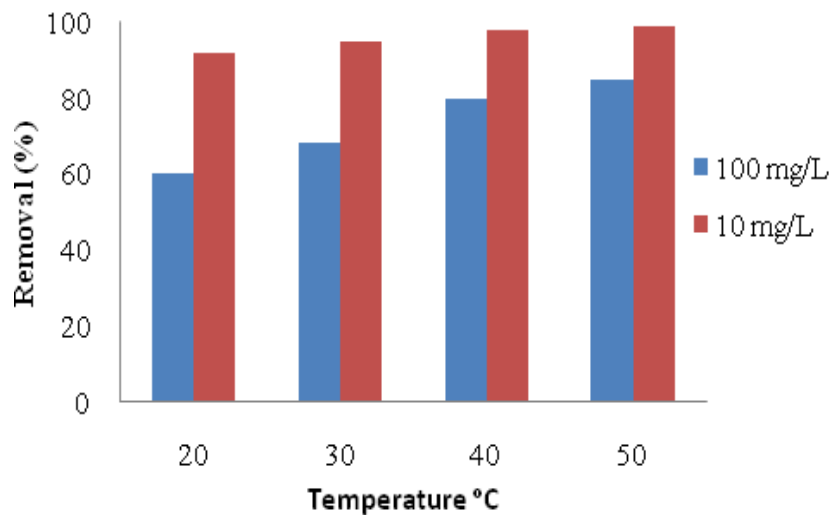


Figure 4. Effect of temperature on MB adsorption

3.5. Adsorption Isotherms

The adsorption equilibrium data for MB onto SBAC were analysed by using a non-linear regression by MATLAB 2014@ to fit the two parameter and three parameter isotherm models. In this work, the Langmuir, the Freundlich and the Redlich–Peterson isotherm models were tested. The correlation coefficient (R^2) and the adjusted correlation coefficient (R^2_{adj}) give the quality of fitting. The statistical indices; the sum squares errors (SSE) and root mean square errors (RMSE) were calculated to evaluate the goodness obtained fits according to the following equations:

$$SSE = (q_{e_{cal}} - q_{e_{exp}})^2 \quad (4)$$

$$RMSE = \sqrt{\frac{\sum (q_{e_{cal}} - q_{e_{exp}})^2}{N}} \quad (5)$$

where $q_{e_{exp}}$ is experimental value of q_e , $q_{e_{cal}}$ is the predicted value of q_e by models, N indicates the number of data points in the experimental run.

The Langmuir isotherm assumes (Langmuir, 1918) that uptake occurs on homogeneous surface by monolayer sorption monolayer adsorption. Langmuir isotherm equation is given as:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mgg^{-1}), C_e the equilibrium concentration of the solute in the bulk solution ($mg l^{-1}$), q_m the maximum adsorption capacity (mgg^{-1}), and K_L is Langmuir isotherm constant ($l mg^{-1}$).

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L , is calculated by the following equation

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Separation factor indicates the nature of adsorption as $0 < R_L < 1$ (favourable). The isotherm parameters, the coefficient of correlation values and the statistical indices were shown in Table 1. The value of R_L was the 0.55 and 0.11 at initial dye concentration $10 mg l^{-1}$ and $100 mg l^{-1}$, respectively, showing that the adsorption of MB on SBAC is favourable. The R_L values decreased with increase in initial dye concentration. This shows that the adsorption process is favourable at higher dye concentration (Mi-Hwa *et al.*, 2010).

The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

where K_F is the Freundlich isotherm constant (Freundlich, 1906) and n represents the adsorption intensity, C_e indicates the equilibrium concentration of adsorbate (mgL^{-1}), q_e is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mgg^{-1}). The model is applicable to the adsorption on heterogeneous surfaces by a uniform energy distribution and reversible adsorption. The magnitude of the exponent n gives an indication on the favorability of adsorption. It is generally stated that values of n in the range $1 < n < 10$ represent good adsorption. The Freundlich isotherm parameters, the correlation coefficient values, SSE and RMSE values were listed in Table 1. The results revealed that there is a good agreement between the experimental and predicted values, suggesting that the Freundlich model is valid for the experimental equilibrium data. Freundlich isotherm is more suitable for the experimental results than is the Langmuir expression because of the lower SSE and RMSE values.

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption:

$$q_e = \frac{k_{RP} C_e}{1 + a_{RP} * C_e^\beta} \quad (9)$$

Where; K_{RP} is the Redlich–Peterson isotherm constant ($l g^{-1}$), a_{RP} is also a constant having unit of $(l mg^{-1})^\beta$, and β is an exponent that lies between 0 and 1. C_e is the equilibrium liquid-phase concentration of the adsorbate ($mg l^{-1}$) and q_e is the equilibrium adsorbate loading onto the adsorbent (mgg^{-1}).

The results present that the SSE and RMSE error values are least while R^2_{adj} and R^2 values approach to one for the Redlich–Peterson model followed by Freundlich and Langmuir models. All the evaluated equilibrium models gave good fit to the experimental data.

Table 1. Parameters of the Redlich- Peterson, Freundlich and Langmuir isotherms for the adsorption of MB dye onto SBAC

Isotherms models	Isotherms parameter	SSE	RMSE	R ² _{adj}	R ²
Langmuir	Q _m (mgg ⁻¹)	6.739	0.2775	0.3041	0.971
	R _L	0.55-0.11			
	K _L (Lmg ⁻¹)	0.08061			
Freundlich	K _F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	1.005	0.07613	0.1593	0.992
	n	2.224			
Redlich- Peterson	K _{RP} (L g ⁻¹)	1.695	0.02333	0.108	0.9963
	a _{RP} (mgL ⁻¹) ^{-β}	1.057			
	β	0.6574			

However the Redlich–Peterson is the best model describing adsorption of MB on the SBAC. The results of this study revealed that best isotherm models fitted for MB adsorption were determined in the order: Redlich–Peterson > Freundlich > Langmuir. Equilibrium isotherms of methylene blue adsorption were previously investigated by other researchers (Hameed and El-Khaiary, 2008; Yener *et al.*, 2008; Tan *et al.*, 2007; Hameed *et al.*, 2007; Tan *et al.*, 2008). The monolayer adsorption capacities of MB on SBAC 6.73 mg g⁻¹. Table 2 lists a comparison of adsorption capacities of methylene blue dye onto different adsorbents.

Table 2 .The adsorption capacity for methylene blue by various adsorbents

Adsorbent	Maximum monolayer Q _m	References
Rice husk activated carbon	28.5	Reddy <i>et al.</i> 2015
Olive stone activated carbon	16.12	Hazzaa and Hussein 2015
Citrus fruit peel carbon	25.51	Dutta <i>et al.</i> 2011
Coir pith carbon	5.87	Kavitha and Namasivayam 2007
Hazelnut shell-activated carbon	8.82	Aygun 2003
Sugarcane bagasse activated carbon	6.73	Present study

3.6. Adsorption kinetics

The pseudo-first-order (PFO) kinetic model(Langergren and Svenska 1898) is given by

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

where q_e and q_t (mg g⁻¹) are the amounts of adsorbate adsorbed at equilibrium and at any time respectively and k_1 (min⁻¹) is the rate constant. The plot of $\ln(q_e - q_t)$ versus t is not shown. The values of k_1 and correlation coefficient, R^2 were listed in Table 2. Although the R^2 values were relatively high ($R^2 > 0.95$) for initial concentration of 10–100mg.L⁻¹, the experimental $q_{e,exp}$ values did not agree with the calculated $q_{e,cal}$ values obtained from the linear plots. This reveals that the adsorption of MB onto the SBAC does not follow PFO kinetic model.

The pseudo-second-order (PSO) model (McKay and Ho 1999) is given as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where k_2 is the rate constant of adsorption (g mg⁻¹min⁻¹). The values of q_e and k_2 are determined from the slope and intercept of the plot of t/q_t against t as shown in Figure 5 and listed in table 2. The correlation coefficient values, R^2 for the second-order kinetic model were almost equal to unity for 10 mg l⁻¹ and 30 mg l⁻¹ concentrations of MB and larger than 0.987 for 50 mg l⁻¹, 70 mg l⁻¹ and 100 mg l⁻¹ concentration of MB.

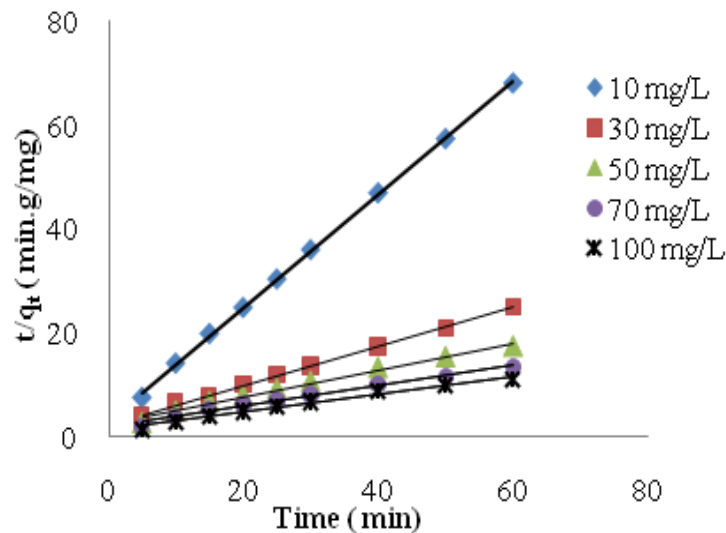


Figure 5: Pseudo-second-order kinetics for adsorption of MB on SBAC

Moreover the calculated $q_{e, cal}$ values agree with the experimental data. This reveals that the adsorption of MB on SBAC follows to the pseudo-second-order kinetic model. These results come in agreement with previous studies (Li, 2013). Table 3 also shows that K_2 decreased with increasing initial concentration of MB. These results agreed with previous studies (Hameed and El-Khaiary, 2008 and Chen *et al.*, 2010). Also the results show that increasing the initial concentration of MB increases the initial adsorption rate ($h = k_2 q_e^2$). Similar results have been previously reported (Belaid *et al.*, 2013). It was stated that the quantity of the rate of adsorption $k_2 q_e$ was exactly the inverse of the half-life of adsorption process ($t_{1/2}$).

Table 3. Kinetics parameters of MB adsorption onto SBAC

C_0 (mg l ⁻¹)	$q_{e, exp}$ (mg g ⁻¹)	PFO			PSO				
		$q_{e, cal}$ (mg g ⁻¹)	K_1 (min ⁻¹)	R^2	$q_{e, cal}$ (mg g ⁻¹)	K_2 g (mg min) ⁻¹	$K_2 q_e$ min ⁻¹	$h=k_2 q_e^2$ mg (g.min) ⁻¹	R^2
10	0.88	0.338	0.066	0.983	0.918	0.373	0.343	0.315	0.999
30	2.4	2.110	0.084	0.966	2.68	0.055	0.147	0.397	0.999
50	3.45	2.316	0.045	0.973	3.861	0.026	0.103	0.398	0.987
70	4.41	2.712	0.041	0.989	4.975	0.020	0.101	0.503	0.987
100	5.5	3.095	0.029	0.964	5.847	0.019	0.116	0.679	0.980

3.7 Adsorption mechanism

Intraparticle diffusion model (Weber and Morris, 1963) was used to describe adsorption mechanism. The intraparticle diffusion model is given as follows

$$q_t = k_{diff} t^{1/2} + C \tag{12}$$

where K_{diff} is the intra-particle diffusion rate constant (mg(gmin)⁻¹), and C_i is a constant indicates the thickness of the boundary layer (m²g⁻¹). The intraparticle diffusion plots of the experimental results, q_t versus $t^{1/2}$ for different adsorbent are shown in Figure 6. The values of K_{diff} , C_i and correlation coefficient R^2 are listed in Table4. The values of C_i obtained from intraparticle diffusion model indicate that thickness of the boundary layer increased by increasing the initial MB concentration and that intraparticle diffusion may not be the controlling factor in the adsorption process. The results revealed that more than one process affected the adsorption and the adsorption process contains both the surface adsorption and intraparticle diffusion. These observations have been reported by others (Yu and Luo, 2014).

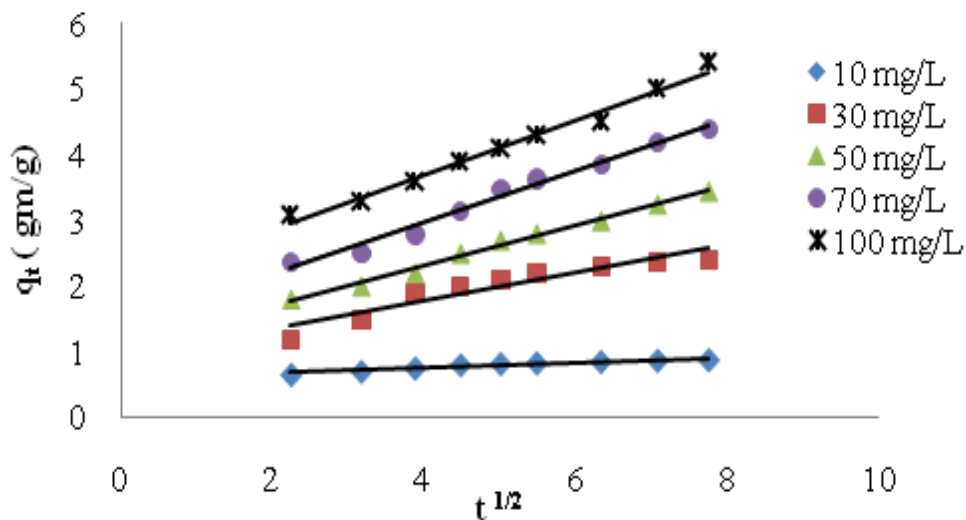


Figure 6. Intraparticle diffusion plot for methylene blue onto SBAC

The film diffusion coefficient (D_f) and pore diffusion coefficient (D_p) are parameters of the kinetic study of the adsorption process. The diffusion coefficients were calculated by method based on adsorption rate proposed. Assuming that the sorbent particles are spherical, half time equations of film and pore diffusions can be calculated from the equations (Anirudhan and Ramachandran, 2014):

$$t_{1/2} = \frac{0.03r^2}{D_p} \quad (13)$$

$$t_{1/2} = 0.23r * \frac{\delta}{D_f} * \frac{C}{C_e} \quad (14)$$

where r is the radius of the adsorbent δ is the film thickness, C and C_e are the concentrations of adsorbate on the adsorbent and in solution at equilibrium state, respectively. The adsorbent was assumed to be in spherical form, and the film thickness is taken as 10^{-3} cm. The film diffusion is the rate limiting step if the values of film diffusion coefficients are in the range of 10^{-6} - 10^{-8} $\text{cm}^2 \cdot \text{s}^{-1}$ but if pore diffusion coefficient is in the range of 10^{-11} - 10^{-13} $\text{cm}^2 \cdot \text{s}^{-1}$, the pore diffusion coefficients will be rate limiting. The results reveal that the magnitude of the coefficient D_f is on the order of 10^{-7} and 10^{-6} $\text{cm}^2 \cdot \text{s}^{-1}$, indicating that film diffusion is the rate limiting step (Anirudhan and Ramachandran, 2014).

Table 4. Intraparticle diffusion parameter and diffusion coefficients values

Concentration mg l^{-1}	K_{diff} $\text{mgg}^{-1}\text{min}^{-1/2}$	C_i (mgg^{-1})	R^2	Film diffusion D_f $\text{cm}^2\text{min}^{-1}$	Pore diffusion D_p $\text{cm}^2\text{min}^{-1}$
10	0.041	0.583	0.924	11.5×10^{-6}	4.10×10^{-6}
30	0.213	0.923	0.891	2.71×10^{-6}	1.76×10^{-6}
50	0.307	1.082	0.992	1.02×10^{-6}	1.20×10^{-6}
70	0.392	1.402	0.983	7.73×10^{-7}	1.19×10^{-6}
100	0.415	2.039	0.984	5.99×10^{-7}	1.33×10^{-6}

3.8 Adsorption thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and the entropy change (ΔS°) can be estimated using equilibrium constants changing with

temperature. The Gibbs free energy change of the adsorption reaction can be determined from the following equation:

$$\Delta G^\circ = -RT \ln KD \quad (15)$$

The KD value was calculated using the following equation:

$$KD = \frac{q_e}{C_e} \quad (16)$$

Relation between ΔG° , (ΔH°) and (ΔS°) can be expressed by the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\ln KD = - \frac{\Delta G^\circ}{RT} = - \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (18)$$

where R (8.314 J mol⁻¹ K⁻¹) is the universal gas constant, T (K) is the absolute solution temperature. According to equation (18), ΔH° and ΔS° parameters are calculated from the slope and intercept of the van't Hoff plot of ln KD versus 1/T, respectively, listed in Table 5. The positive ΔH° value obtained indicated that the adsorption process was endothermic in nature, which is in agreement with the experimental observations.

Table 5. Thermodynamic parameters for adsorption of MB onto SBAC

Parameters	Temperature K			
	293	303	313	323
ΔG° kJ mol ⁻¹	4.621388	3.901681	2.384447	1.525277
ΔH° kJ mol ⁻¹	36.32387			
ΔS° J mol ⁻¹ K ⁻¹	107.8326			
R ²	0.984			

Similar phenomena had been previously reported by other authors (Wang and Zhu, 2007). The positive values of ΔS° obtained showed the affinity of the SBAC for MB and the increasing randomness at the solid–solution interface and the positive values of ΔG° obtained indicated the non-spontaneous nature of the adsorption process at the range of temperatures being studied.

4. Conclusions

Activated carbon has been prepared from sugarcane bagasse for removal of methylene blue dye from aqueous solutions. The maximum removal of methylene blue was attained at pH 7. The adsorption equilibrium was reached within 60 and 120 min for initial dye concentration 10 mg l⁻¹ and 100mg l⁻¹ respectively. The three-parameter isotherm models as well as two-parameter models were found to be applicable for the adsorption equilibrium data by non-linear regression. The Redlich–Peterson is the best model describing adsorption of MB on the SBAC. The SSE and RMSE error values are least and R² values approach to one. The adsorption process is governed by the pseudo-second order reaction, at various initial dye concentrations. Thermodynamic studies indicated that the adsorption process is endothermic. The results indicated that sugarcane bagasse activated carbon could be used as a low-cost adsorbent for the removal of methylene blue from wastewater.

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