



Removal of methylene blue dye from aqueous solutions by using date stones derived as an activated carbon

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ABSTRACT

In this study, activated carbon (DSAC) was prepared from date stones using sulfuric acid activation, an inexpensive material, showed accepted scavenging behaviour through adsorption for the removal of methylene blue (MB) from aqueous solution. Batch adsorption studies were conducted to evaluate the effects of initial concentration (5–100 mg L⁻¹), pH (2.5–10), adsorbent dose (0.25–3 g.L⁻¹) and effect of temperature (10–55 °C). It was found that pH plays a major role in the adsorption process; adsorption capacity was influenced by the physical and surface chemical properties of carbon and the pH of the solution. The experimental data were analyzed by three different types of isotherm models, the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm at different temperatures. The experimental results fitted well with the Freundlich and Tempkin adsorption isotherm, indicating thereby multilayer adsorption of the dye. Change in Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH) were also calculated from the adsorption results were found the adsorption process was endothermic.

Keywords: Adsorption; methylene blue, isotherm; endothermic.

INTRODUCTION

Textile industries consume large amount of water mainly for dyeing and finishing processes. Although textile effluent is not highly toxic, the colored nature of textile wastewater causes major environmental problems especially toward the aquatic ecosystem[1]. The discharge of dye effluents from textile, leather, paper and plastic industries into the environment poses severe problems to many forms of life. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood, and silk[2].

Methylene blue has wider application, which includes coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. Though methylene blue is not strongly hazardous but on inhalation, it can show various harmful effects. It can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea and gastric problem [3, 4]. Different methods were used for dyes removal, one of them is adsorption method. Adsorption has been found to be superior to other techniques for water re-use in

terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [5, 6].

Activated carbon has been widely using for this purpose because of its high adsorption capacity. However, its high cost sometimes tends to limit its use. Several nonconventional, low-cost adsorbents have also been tried for dye removal. Physical and chemical activation are the common methods for production of activated carbons. Physical activation involves carbonization or pyrolysis of the carbonaceous materials at elevated temperatures (500–900 °C) in an inert atmosphere, followed by thermal activation at the same temperatures or as per pyrolysis or at a high temperature in the presence of oxidizing gas such as steam, air and carbon dioxide[7]. By chemical activation it is possible to prepare activated carbon in a single step process. The activation is based on the decomposition of precursor with a chemical activator such as KOH, K₂CO₃, NaOH, ZnCl₂, H₂SO₄ and H₃PO₄ etc., at elevated temperatures [8-14] .In this study, activated carbon was produced from Date Stone by sulfuric acid activation method and methylene blue (MB) adsorption ability of the prepared (DSAC) was examined in batch adsorption technique. Effective parameters such as initial pH of methylene blue (MB) solution, activated carbon dosage and temperature were investigated.

MATERIALS AND METHODS

Materials: The methylene blue used in this work was purchased from Sigma–Aldrich. The MB was chosen in this study because of its known strong adsorption onto solids. MB has a molecular weight of 373.90 g mol⁻¹, chemical structure of MB dye was shown in fig.1 and the maximum wavelength of this dye is 663 nm.

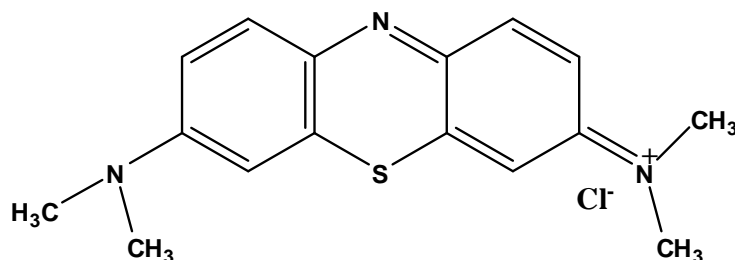


Fig. 1: Chemical Structure of Methylene Blue.

Date stones were collected as waste materials. The date stones are water washed and dried at 105°C in a hot oven until it is completely dry, which are then crushed, sieved to size 2.0 to 2.5 mm and stored in airtight containers for further experimentation. Analytical grade Methylene blue (MB) supplied by Sigma-Aldrich, is used as adsorbate without further purification. The concentration of this dye is determined using a uv-visible spectrophotometer at 663 nm wavelength.

Preparation of date stones activated carbon (DSAC): 50 g of dried of date stones impregnated with 50 mL of 10 % (wt/wt) H₂SO₄ solution, so it has to have an impregnation ratio of 1:5 (wt. H₂SO₄: wt. date stones). The H₂SO₄ soaked sample is left overnight and the excess water is evaporated in an oven at 100°C to ensure complete absorbance of the H₂SO₄ on to the date stones powder. The acid soaked samples are semi-carbonized in a hot air oven at a preset furnace temperature of 500°C for 2 h under a self-generated atmosphere. After activation, the samples are washed repetitively with distilled water to remove residual acid. The product is finally air dried at 105°C, before being manually ground to a fine powder and sieved to a size below 75 µm, which are utilized for product characterization.

Effect of DSAC adsorbent dose on the MB adsorption: To study the effect of DSAC dose on the MB adsorption, different amounts of DSAC (0.025, 0.075, 0.1, 0.2, 0.25, and 0.3 g) were added into a number of 250-mL stoppered glass (Erlenmeyers flasks) containing a definite volume (100 mL in each flask) of fixed initial concentration (30 mg L⁻¹) of dye solution without changing the solution pH at 30 °C. The

flasks were placed in a thermostated water bath shaker (Protech, Malaysia) and agitation was provided at 120 rpm for 60 min and the dye concentrations were measured at equilibrium.

Effect of solution pH: In this study, the effect of solution pH on adsorption of MB on DSAC was studied by mixing 0.1 g of DSAC with 100 mL of dye solution of 30 mg L⁻¹ initial concentration at different pH values (2.5–10.0) and 30 °C. The pH was adjusted with 0.1N NaOH and 0.1N HCl solutions and measured by using a pH meter. Agitation was made for 60 min at a constant agitation speed of 120 rpm. The dye concentrations were measured by a double beam UV–VIS spectrophotometer at 663 nm wavelength. Prior to the measurement, a calibration curve was obtained by using the standard MB solution with the known concentrations.

Equilibrium studies : Batch adsorption experiments were carried out by adding a fixed amount of sorbent (0.1 g) into a number of 250-mL stoppered glass (Erlenmeyers flasks) containing a definite volume (100 mL in each case) of different initial concentrations (5–100 mg L⁻¹) of dye solution without changing pH and temperatures (10, 30, and 55 °C). The flasks were placed in a thermostatic water bath shaker and agitation was provided at 120 rpm for 60 min to ensure equilibrium was reached. The amount of adsorption at equilibrium, q_e (mg g⁻¹), was calculated by equation (1)

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L), and m is the mass of dry adsorbent used (g).

Also the percentage of dye removed ($R\%$) from solution was calculated using the following equation

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Mass dosage: In order to provide quantitative adsorbate uptake determination of ideal adsorbent dosage is demanded. Commonly increasing adsorbent dosages improve adsorption efficiencies. This can be explained by the increase of surface area where the adsorption takes place. Under the conditions of pH of dye solution (pH 6.1), C_0 of 30 mg L⁻¹, Temp. 30 °C and contact time of 60 min., the effect of dose of activated carbon (DSAC) on the percentage removal and adsorption capacity of methylene blue (MB) is shown in fig. 2. It is apparent that the percentage removal of methylene blue (MB) was increased by increasing the activated carbon dose. This was the reason that the number of available adsorption sites was increased by increasing the adsorbent dose. Increases in the percentage of dye removal with adsorbent masses could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption, as already reported in several papers.[15-17].

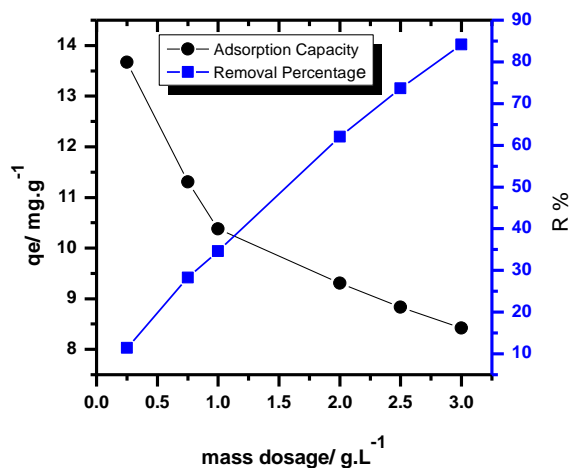


Fig. 2: Effect of mass dosage on the adsorption of methylene blue (MB) by the surface of DSAC. (pH of solution 6.1, Temp. 30 C, dye concentration 30 ppm, agitation rate 120 rpm, time of agitation 1 hr.)

From Fig. 2 shows the removal of MB by DSAC at different dosage of adsorbent (0.025–0.33 g) at initial concentration of 30 mg L^{-1} dye solution and Temp. 30°C . From the Fig. 2, it was observed that, the percentage of dye removal increased from 11.34 to 84.12 % with an increase in adsorbent mass from 0.025 to 0.3 g. The percentage removal increased with the DSAC dosage up to a certain limit and then it reached a constant value.

Effect of pH: The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of different pollutants. Change of pH affects the adsorptive process through dissociation of functional groups of the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. Therefore the pH of the solution appears to be a strong factor affecting the adsorption characteristics of Methylene blue (MB) onto DSAC as it controls the electrostatic interaction between DSAC and the Methylene blue (MB) molecules [2, 18]. In this study, impact of pH has been investigated by adjusting pH of the dye solutions from 2.5 to 10. In the conducted experiments, 0.1 g activated carbon has been added into 100 mL of 30 mg L^{-1} dye solution. Samples have been shaken for 60 min in 120 rpm agitation speed at 30°C , the obtained results are given in fig.3

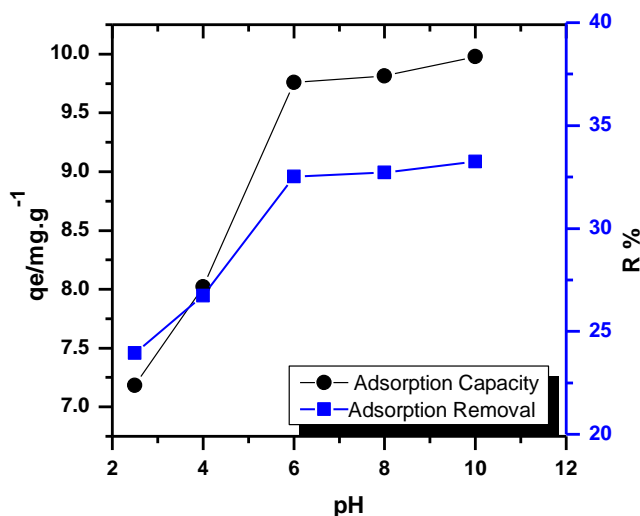


Fig. 3: Effect of pH on the adsorption of Methylene blue (MB) by the surface of DSAC. (Mass dosage 0.1 gm, Temp. 30°C , dye concentration 30 ppm, agitation rate 120 rpm, time of agitation 1 hr.)

Initially, it seems increasing pH of the dye solution 2.5 – 10, yields an increase the adsorption capacity of DSAC (fig. 3), the sharp increasing in adsorption of Methylene blue (MB) ions was observed at the pH increase 2.5 – 6. With further increase in pH, adsorption is slightly increased and continues till the pH of 10. At strongly acidic media remarkable electrostatic repulsion exists between the positively charged surface of the used adsorbent and cationic dye molecules [18], this is due to zero point charge effect of the surface and also ionization state of methylene blue dye, because the surface will have high positive charge density, and, under these conditions, the uptake of methylene blue (MB) would be quite low because of electrostatic repulsion [19].

Adsorption Isotherm: The adsorption isotherm describes how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. It can provide qualitative information on the nature of the solute–surface interaction at constant temperature. [20]. Equilibrium studies have been performed at three different temperatures and data were fitted to three different adsorption isotherm models viz., Langmuir adsorption isotherm model, Freundlich adsorption isotherm model, and Tempkin adsorption isotherm model. Results are shown in fig. 4, the values of equilibrium constants are found out and shown in Table 1.

Table 1: Experimental constants for the adsorption isotherms models under study.

Isotherm models	Parameters	Temp./283 K	Temp./303 K	Temp./333 K
Langmuir $q_e = \frac{K_L q_{max} C_e}{1 + K_L C_e}$	q_{max}	9.62261	12.62325	15.70565
	K_L	3.88916	0.4445	1.36616
	R^2	0.5542	0.5279	0.67239
Freundlich $q_e = K_F C_e^{1/n}$	K_F	5.83951	6.59092	9.64678
	$1/n$	0.14631	0.15671	0.13028
	R^2	0.94726	0.97612	0.99525
Tempkin $q_e = \frac{RT}{b} \ln(k_T C_e)$	K_T	1.10702	1.13993	1.12177
	B^*	1.07584	1.2357	1.2439
	R^2	0.9745	0.97216	0.97969

q_{max} =maximum adsorption capacity; K_L = Langmuir constant; K_F , $1/n$ = Freundlich constants; b , k_T = Tempkin constants; R = universal gas constant; T = absolute solution temperature in Kelvin.. $B^* = \frac{RT}{b}$

In order to describe the uptake of dyes by adsorbent, the isotherms data were analyzed using non-linear theoretical models and non-linear fitting method. The two and three parameters models, namely Langmuir, Freundlich, and Tempkin equations were applied to evaluate the fit by isotherm for the adsorption of dyes, results are shown in fig.4. The general form of the **Langmuir** isotherm is[23]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where K_L (L mg⁻¹) is a constant and C_e is the equilibrium concentration (mg L⁻¹), q_e is the amount of dye adsorbed per gram of adsorbent (mg g⁻¹) at equilibrium concentration C_e , and q_m is the maximum amount of solute adsorbed per gram of sorbent (mg g⁻¹), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of dye adsorption increases as the concentration increases up to a saturation point [22].

The **Freundlich** empirical model is represented by [23]:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where K_F (mg^{1-1/n} L^{1/n} g⁻¹) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple. The parameter n is related to the adsorption energy distribution, and K_F indicates the adsorption capacity.

The derivation of the **Tempkin** isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm is[24]:

$$q_e = \frac{RT}{B} \ln(K_T C_e) \quad (5)$$

Where K_T is the equilibrium binding constant, corresponding to the maximum binding energy, and constant b is related to the heat of adsorption. This can also be concluded from the Freundlich model fitting results. The magnitude of the exponent, $1/n$, gives an indication of the favourability of adsorption. Value of $n > 1$ represents favourable adsorption condition [25]. The Tempkin model and Freundlich model fitted the experimental data better than Langmuir model, indicating the adsorption of methylene blue (MB) onto the adsorbent tended to multilayer adsorption. The R^2 of the three models descend in the order of: Freundlich > Tempkin > Langmuir.

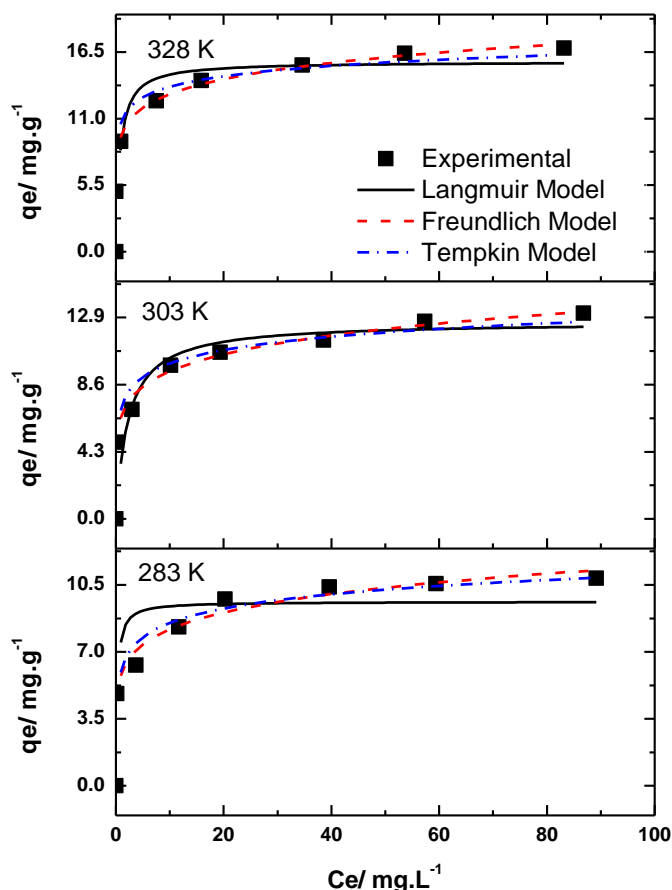


Fig. 4: Fits for the adsorption isotherms model at different temperatures (Exp. Conditions: pH 6.1, mass dosage 0.1 gm, particle size 75 μm , and Temp. 30 $^{\circ}\text{C}$)

Thermodynamic study: The thermodynamic parameters, including the free energy changes (ΔG^0), standard enthalpy changes (ΔH^0) and the entropy changes (ΔS^0) associated with the adsorption process can be used to deduce the adsorption mechanism. They can be calculated by the dependence of thermodynamic equilibrium constant (K_c) on temperatures [26]

$$\Delta G^0 = -RT \ln K_c \quad (6)$$

$$\ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

The thermodynamic equilibrium constant (K_c) for the adsorption of MB on DSAC can be calculated [20]:

$$K_c = \frac{C_{ads}}{C_e} \quad (8)$$

In Eq. (8), K_c represents the equilibrium constant, C_{ads} shows the amount of dye adsorbed on activated at equilibrium (mg/g) and C_e is equilibrium concentration of dye (mg L $^{-1}$). According to equation. (6), the values of ΔG^0 were calculated and listed in Table 2. The values of ΔG^0 of dye DSAC adsorption systems are all negative, which indicates the spontaneous adsorption processes. Moreover, the increase in the absolute value of ΔG^0 with increasing temperature indicates that higher temperatures facilitated the adsorption. The value of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the van't Hoff plot (fig.5) of $\ln K_c$ against $1/T$, respectively, and the results are listed in table 2. The positive value of

ΔH^0 indicates that the adsorption processes are endothermic. When attraction between adsorbates and an adsorbent took place, the change in standard enthalpy was caused by various forces, including van der Waals, hydrophobicity, hydrogen bonds, ligand exchange, dipole-dipole interactions and chemical bonds.

Table 2: Thermodynamics parameters for dye adsorption of MB dye by DSAC surface.

Temp/ K	K_c	$\Delta G^0/ \text{kJ.mol}^{-1}$	$\Delta H^0/ \text{kJ.mol}^{-1}$	$\Delta S^0/ \text{J.K}^{-1}\text{mol}^{-1}$
283	131.0714	-11.4719	6.9538	65.0038
303	153.5714	-12.6818		
328	196.4286	-14.3993		

From table 2 shows the negative ΔG values indicate thermodynamically spontaneous nature of the adsorption. The decrease in ΔG values with increasing temperature shows a decrease in feasibility of adsorption at higher temperatures. The positive ΔH is an indicator of endothermic nature of the adsorption and also its magnitude gives information on the type of adsorption, which can be either physical or chemical. The enthalpy of adsorption, was 6.9 kJ mole^{-1} corresponds to a physical sorption. Physical adsorption occurs when the intermolecular attractive forces between molecules of adsorbate and adsorbent are greater than those between molecules of the adsorbate itself. Physical adsorption, which may be a mono-molecular or multi-molecular layer, occurs rapidly. In contrast, chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent. In this study, the adsorption heat of MB is in range of physisorption. Therefore, the ΔH values show that the adsorption of MB on DSAC was taken place via physisorption. The positive ΔS value suggests an increase in the randomness at adsorbate-solution interface during the adsorption process.

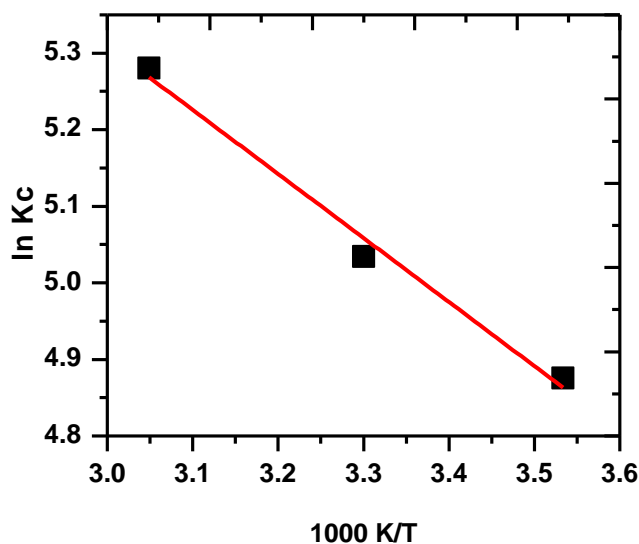


Fig. 5. Van't Hoff plot for the adsorption of MB dye by DSAC (pH 6, mass dosage $0.1 \text{ g } 100 \text{ mL}^{-1}$, contact time 60 min., and agitation speed 120 rpm, particle size 75 μm).

APPLICATIONS

The activated carbon prepared from date stones, an inexpensive material, showed accepted scavenging behaviour through adsorption for the removal of methylene blue (MB) from aqueous solution.

CONCLUSIONS

Sulfuric acid has been used as an activator for preparation of activated carbon from date stones. Equilibrium adsorption data of MB onto DSAC were well represented by Freundlich and Tempkin isotherm model with high presented of R^2 value. Removal of methylene blue (MB) from aqueous solution by adsorption onto DSAC was investigated at three different temperatures. The adsorption reaction was endothermic with the increasing of the randomness at the solid/liquid interface during the adsorption. As a result of the thermodynamic evaluation of MB adsorption, the obtained negative ΔG values revealed that the adsorption of MB onto DSAC was thermodynamically feasible and spontaneous, the positive values of ΔH suggested the endothermic nature of adsorption, and the positive values of ΔS indicated the increasing randomness at the solid/solution interface during the adsorption process.

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