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REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION BY ACTIVATED CARBON PREPARED FROM THE PEEL OF CUCUMIS SATIVA FRUIT BY ADSORPTION

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The use of low-cost, locally available, highly efficient, and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. This study investigates the potential use of activated carbon prepared from the peel of *Cucumis sativa* fruit for the removal of methylene blue (MB) dye from simulated wastewater. The effects of different system variables, adsorbent dosage, initial dye concentration, pH, and contact time were investigated, and optimal experimental conditions were ascertained. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. The optimum pH for dye adsorption was 6.0. Maximum dye was sequestered within 50 min of the start of each experiment. The adsorption of methylene blue followed the pseudo-second-order rate equation and fit the Langmuir, Freundlich, Dubinin-Radushekevich (D-R), and Tempkin equations well. Maximum removal of MB was obtained at pH 6 as 99.79% for adsorbent doses of 0.6 g/ 50 mL and 25 mg/L initial dye concentrations at room temperature. The maximum adsorption capacity obtained from the Langmuir equation was 46.73 mg g^{-1}. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation ($R^2 > 0.9677$) with intraparticle diffusion as one of the rate-determining steps. Activated carbon developed from the peel of *Cucumis sativa* fruit can be an attractive option for dye removal from wastewater.

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INTRODUCTION

The effluents from the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution (Bhatnagar et al. 2004). Many dyes and their breakdown products may be toxic for living organisms (Kannan et al. 2001). Therefore, decolorization of dyes is an important aspect of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems (Kargi et al. 2004). Generally, biological aerobic wastewater systems are not successful for decolorization of the majority of dyes (Kannan et al. 2001).

Color removal has been extensively studied using such physco-chemical methods as coagulation, ultra-filtration, electro-chemical adsorption, and photo-oxidation (Kannan et al. 2001; Bhattacharyya et al. 2005). Among these methods, adsorption is widely used for dye removal from wastewaters (Bhattacharyya et al. 2005; Walker et al. 1998). Granulated activated carbon (GAC) or powdered activated carbon (PAC) is commonly used for dye removal (Walker et al. 1998; Chern and Wu 2001; Namasivayam et al. 1996). However, these products are expensive, and their regeneration or disposal has several problems. Thus, the use of several low-cost adsorbents has been studied by many researchers. They have studied the feasibility of using low-cost materials, such as waste orange peel (Namasivayam et al. 1998), banana pith (McKay et al. 1986), cotton waste, rice husk (Ramakrishna and Viraraghavan 1997), bentonite clay (Dogan et al. 2004), neem leaf powder (Walker et al. 1998), powdered activated sludge (Bhattacharyya et al. 2005), perlite (Waranusantigul et al. 2003), bamboo dust, coconut shell, groundnut shell, rice husk, and straw (Kannan et al. 2001), duck weed (Otero et al. 2003), and sewage sludge (Mc-Kay et al. 1985) as adsorbents for removal of various dyes from wastewaters.

Cucumis sativa is a local fruit available in abundance throughout the year. The peel of *Cucumis sativa* fruit, which is removed before consumption, is a waste product that is usually discarded. Local vendors at a railway level crossing (near Eachnari, Coimbatore, Tamil Nadu) sell about 600 to 700 kg of the fruit every day at this one locale, and about 3% of this accounts as waste. Since the peel of *Cucumis sativa* fruit is available free of cost, only its carbonization would be required for waste water treatment. Therefore the main objective of this study was to evaluate the possibility of using dried peel of *Cucumis sativa* fruit to develop a new low-cost activated carbon and study its application to remove methylene blue from simulated wastewater. The peel of *Cucumis sativa* fruit was previously investigated to adsorb cationic dyes (Santhi et al. 2009). Systematic evaluation was carried out of parameters such as pH, adsorbent dose, adsorbent particle size, initial dye concentration, and time.

MATERIALS AND METHODS

Preparation of Activated Carbon from Peel of Cucumis Sativa Fruit (CCS)

The peel of *Cucumis Sativa* fruit was obtained from local vendors at Eachnari railway Gate, Coimbatore District (Tamil Nadu). The dried peel of *Cucumis sativa* fruit biomass was added in small portions (1.0 kg) to 1000 mL of 98% H_2SO_4 for 12 hours, washed thoroughly with distilled water until it attained neutral pH, and soaked in two percent $NaHCO_3$ overnight in order to remove any excess acid present. Then the material was washed with distilled water and dried at 110 ± 2^0C. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators until use.

Preparation of synthetic solutions

A stock solution of 500 mgL^{-1} was prepared by dissolving the appropriate amount of MB (obtained from s.d. Fine Chemicals, Mumbai, India) in 100 mL and made to 1000 mL with distilled water. Different concentrations ranging between 25 and 200 mg L^{-1} of MB were prepared from the stock solution. All the chemicals used throughout this study

were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH was adjusted with 0.1 M HCl or 0.1 M NaOH. All the adsorption experiments were carried out at room temperature (27 ±2°C).

Batch Adsorption Studies

Effect of pH on MB adsorption

The effect of pH on the equilibrium uptake of dyes was investigated by employing an initial concentration of MB of 100mg/L and 0.2 g/50 mL of CCS. The initial pH values were adjusted with 0.1 M HCl or NaOH to form a series of solutions having pH values from 2 to 10. The suspensions were shaken at room temperature (27 ±2°C) using an agitation speed of 150 rpm. The minimum contact time required to reach the equilibrium (110 min) and the amount of MB adsorbed were determined.

Effect of CCS dose on MB adsorption

The effect of adsorbent dose on the equilibrium uptake of MB (100 mg L^{-1}) was investigated with CCS concentrations of 0.2, 0.4, and 0.6 g/ 50mL. The experiments were performed by shaking known MB concentrations with the different CCS concentrations shown above to the equilibrium uptake (110 min), and the amount of MB adsorbed was determined.

Kinetic studies

Adsorption studies were conducted in 250-mL shaking flasks at a solution pH of 6.0. The CCS (0.2g/50mL) was thoroughly mixed individually with 50mL of MB solution (50, 100, 150, and 200 mg/L), and the suspensions were shaken at room temperature. Samples of 1.0 mL were collected from the duplicate flasks at required time intervals viz.10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 110 min and were centrifuged for 5 min. The clear solutions were analyzed for residual MB concentration in the solutions.

Adsorption isotherm

Batch adsorption experiments were carried out in a rotary shaker at 150 rpm using 250mL-shaking flasks at room temperature for 110 min. The CCS (0.2 and 0.6 g) was thoroughly mixed with 50 mL of MB solutions. The isotherm studies were performed by varying the initial MB concentrations from 25 to 200 mg/L at pH 6.0. The pH was adjusted using 0.1 M HCl or 0.1 M NaOH before addition of CCS and maintained throughout the experiment. After shaking the flasks for 110 min, the reaction mixture was analyzed for the residual MB concentration.

The concentration of MB in solution was measured by a direct UV-vis spectro-photometric method using a Systronic Spectrophotometer-104 at a wavelength of 480 nm. All experiments were duplicated, and only the mean values are reported. The maximum deviation observed was less than ±4%.

Adsorption of MB from simulated wastewater was studied using 0.2g / 50 mL of CCS and MB concentrations of 100 mg /L at an initial pH 6.0. The amount of dye adsorbed at equilibrium onto carbon, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_o - C_e) \, V/W \tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium liquid-phase concentration of MB, respectively, V the volume of the solution(L), and W is the weight of the CCS used(g).

RESULTS AND DISCUSSION

Effect of System pH on MB Uptake

The pH of the system exerted a profound influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Figure 1 shows the variations in the removal of dye from wastewater at different system pH. From the figure, it is evident that the maximum removal of MB color was observed at pH 6. A similar trend of pH effect was observed for the adsorption of methylene blue on activated carbon prepared from fly ash (Tabrez et al. 2009), natural Jordanian tripoli (Alzaydien 2009), and biosolids (Sarioglu and Atay 2006). This result may be attributed to the hydrophobic nature of the developed carbon, which led to absorption of hydrogen ions (H^+) onto the surface of the carbon when immersed in water, making it positively charged. A low pH value (1.0 to 3.0) leads to an increase in the H^+ ion concentration in the system, and the surface of the activated carbon acquires a positive charge by absorbing H^+ ions. On the other hand, an increase of the pH value (6) led to an increase of the number of negatively charged sites. As the CCS surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecules, leading to maximum adsorption of MB (El Nemr et al. 2009) from waste water. The lowest adsorption occurred at pH 2.0, and the highest adsorption occurred at pH approximately 6.0. The adsorbent's surface would be positively charged up to pH < 4, and heterogeneous in the pH range 4-6. Thereafter, it should be negatively charged. Moreover, the increasing adsorption of MB with increasing of pH value is also attributed to the attraction between cationic dye and excess OH^- ions in the solution. The pH at the zero point of charge (pH_{zpc}) of the CCS is reported to be 4.0.

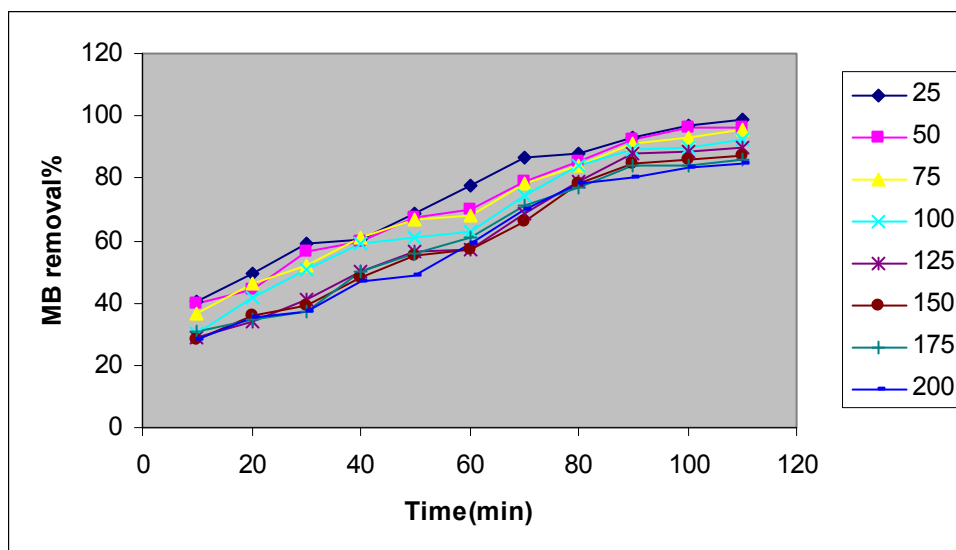### Effect of Contact Time and Initial MB Concentration

The relation between removal of MB and reaction time was studied. The results of percentage removal of MB at pH 6.0 with increase of contact time using CCS are presented in Fig. 2. It was found that more than 50% removal of MB concentration occurred in the first 10 min, and thereafter the rate of adsorption of the MB onto CCS was slow. The rapid adsorption at the initial contact time is attributed to the highly negatively charged surface of the CCS for adsorption of cationic MB in the solution at pH 6. The later slow rate of MB adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species onto the surface of CCS and the available cationic adsorbate species in the solution, as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent. The equilibrium was attained at 110 min when the maximum MB adsorption onto CCS was reached.
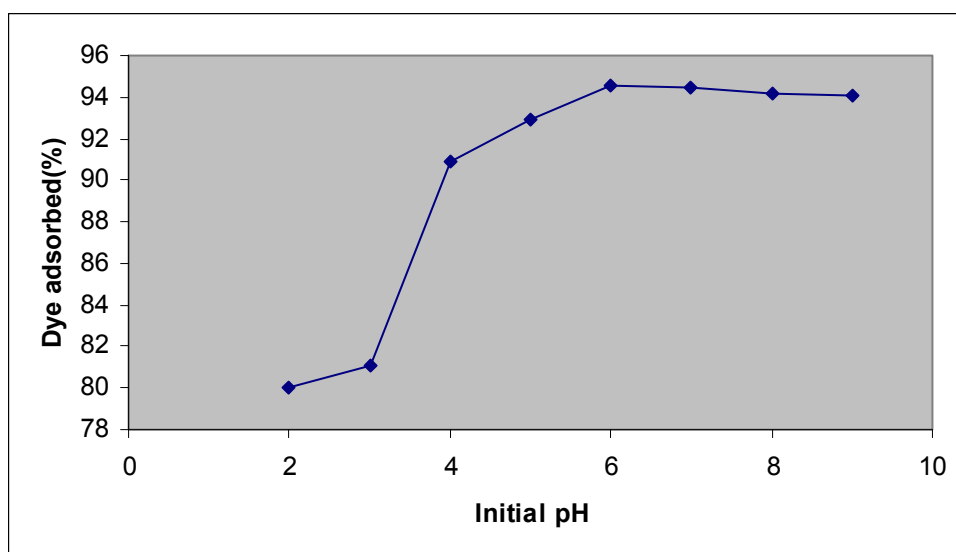
Fig. 1. Effect of system pH on adsorption of MB (100 mg L^{-1}) onto CCS (0.2 g /50mL) at room temperature (27 ± 2 °C), agitation speed 150 rpm for the minimum contact time required to reach the equilibrium (110 min).

Also, the effect of initial concentration of MB in the solution on the capacity of adsorption onto CCS was studied and results are shown in Fig. 2. The experiments were carried out at a fixed adsorbent dose (0.2 g/50 mL) in the test solution at room temperature (27 ± 2 °C), pH 6 and at different initial concentrations of MB (25, 50, 75, 100, 125, 150, 175, and 200 mgL^{-1}) for different time intervals (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 110 min). Figure 2 shows that the percentage of adsorption efficiency of CCS decreased with the increase of initial MB concentration in the solution. Though the percent adsorption decreased with increase in initial dye concentration, the actual amount of MB adsorbed per unit mass of adsorbent increased with increase in MB concentration in the test solution.

It is evident from Fig. 2 that the amount adsorbed on the solid phase CCS at a lower initial concentration of MB was smaller than the corresponding amount when higher initial concentrations were used. However, the percentage removal of MB was greater at lower initial concentrations and smaller at higher initial concentrations. The adsorption capacity for CCS was increased from 6.178 to 42.4 mg g^{-1} as the MB concentration increased from 25 to 200 mg L^{-1}. In the process of MB adsorption initially dye molecules have to first encounter the boundary layer effect, then they have to diffuse from the boundary layer film onto adsorbent surface, and then finally they have to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time.

Fig. 2. Effect of contact time on the removal of different initial concentrations of MB using CCS (0.2 g/50mL) at pH 6.0

Effect of Adsorbent Mass on MB Adsorption

The adsorption of MB on CCS was studied by changing the quantity of adsorbent (0.2, 0.3, 0.4, 0.5, and 0.6 g/50 mL) in the test solution while keeping the initial MB concentration (100 mg L^{-1}), temperature (27 ± 2 ^{o}C), and pH (6.0) constant at contact times for 110 min (Fig. 3). The adsorption increased from 92.53% to 98.07% as the CCS dose increased from 0.2 g to 0.6 g/50 mL at the equilibrium time (110 min). Maximum MB removal was achieved within 10 to 50 min, after which MB concentration in the reaction solution was almost constant. The increase in the adsorption with adsorbent dose can be attributed to increased MB surface area and availability of more adsorption sites, while the unit adsorbed of MB decreased with increase in CCS dose.

Isotherm Data Analysis

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.
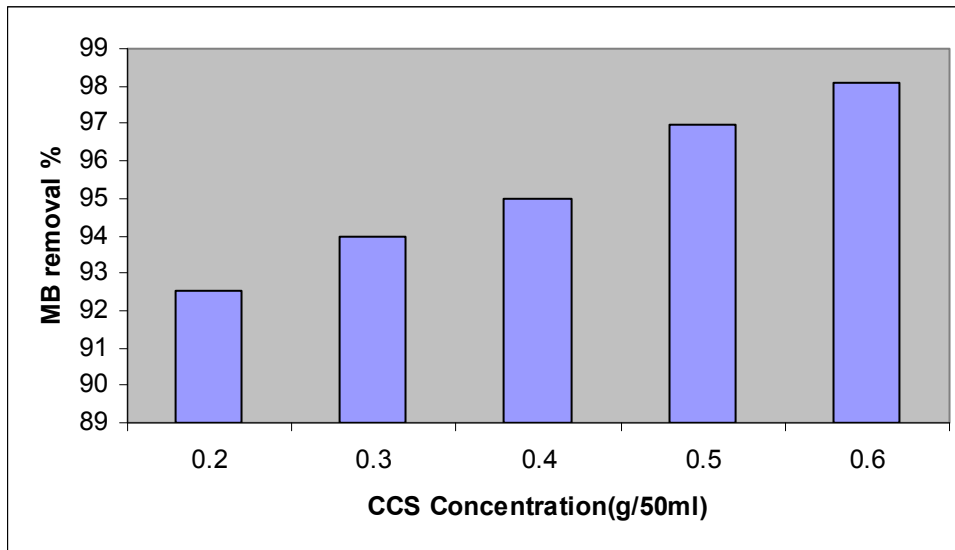
Fig. 3. Effect of adsorbent concentration on MB removals (C_0: 100 mg L^{-1}, pH 6.0, agitation speed: 150 rpm, temperature: 27 ± 2 °C)

Langmuir isotherm

The theoretical Langmuir isotherm (Langmuir 1916) is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface (Doğan et al. 2000). Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \tag{2}$$

In Eq. (2), C_e and q_e are as defined before in Eq. (1); Q_m is a constant and reflects a complete monolayer (mg g^{-1}); K_a is adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption. The Langmuir isotherm Eq. (2) can be linearized into the following form (Kinniburgh 1986; Longhinotti et al. 1998):

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \tag{3}$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$.

The results obtained from the Langmuir model for the removal of MB onto CCS are shown in Table 1. The correlation coefficients reported in Table 1 showed strong positive evidence on the adsorption of MB onto CCS, following the Langmuir isotherm.

The applicability of the linear form of the Langmuir model to CCS was proven by the high correlation coefficients, $R^2 > 0.98$. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Q_m obtained from the Langmuir is 46.73 mg g^{-1}.

The Freundlich isotherm

The Freundlich isotherm model (Freundlich 1906) is the earliest known equations describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation,

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

where K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm, while $1/n$ above 1 is indicative of cooperative adsorption. Equation (4) can be linearized in the logarithmic form (Eq.(5), and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of the MB onto CCS is presented in Table 1. The correlation coefficients (>0.98) showed that the Freundlich model is comparable to the Langmuir model. The $1/n$ is lower than 1.0, indicating that MB is favorably adsorbed by CCS.

The Tempkin isotherm

Tempkin adsorption isotherm model was used to evaluate the adsorption potentials of the CCS for MB. 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 Tempkin isotherm has commonly been applied in the following form (Aharoni and Sparks 1991; Aharoni and Ungarish 1977; Wang and Qin 2005):

$$q_e = \frac{RT}{b} \ln(AC_e) \qquad (6)$$

The Tempkin isotherm Eq. (6) can be simplified to the following equation,

$$q_e = \beta \ln \alpha + \beta \ln C_e \tag{7}$$

where $\beta = (RT)/b$, T is the absolute temperature in Kelvin, and R is the universal gas constant, 8.314 J (mol K)$^{-1}$. The constant b is related to the heat of adsorption (Akkaya and Ozer 2005; Pearce et al. 2003). The adsorption data were analyzed according to the linear form of the Tempkin isotherm equation (7). Examination of the data shows that the Tempkin isotherm fit well to the MB adsorption data for CCS. The linear isotherm constants and coefficients of determination are presented in Table 1. The correlation coefficients R^2 obtained from Tempkin model were comparable to those obtained for the Langmuir and Freundlich equations, which indicates the applicability of Tempkin model to the adsorption of MB onto CCS.

The Dubinin-Radushkevich (D-R) isotherm
The D–R model was also applied to estimate the porosity apparent free energy and the characteristics of adsorption (Dubinin 1960, 1965; Radushkevich 1949). The D–R isotherm does not assumes a homogeneous surface or constant adsorption potential. The D–R model has commonly been applied in the following Eq. (8), and its linear form can be shown in Eq. (9),

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{8}$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{9}$$

where K is a constant related to the adsorption energy, Q_m is the theoretical saturation capacity, and ε is the Polanyi potential, calculated from Eq. (10).

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{10}$$

The slope of the plot of $\ln q_e$ versus ε^2 gives K (mol^2 (kJ^2)$^{-1}$), and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation (Kundu and Gupta 2006):

$$E = \frac{1}{\sqrt{2K}} \tag{11}$$

The calculated values of D–R parameter are given in Table 1. The saturation adsorption capacity Q_m obtained using the D–R isotherm model for adsorption of MB onto CCS is 26.36 mg g^{-1} at 0.2g / 50 mL asorbent dose, which is close to that obtained (15.48 mg g^{-1}) from Langmuir isotherm model (Table 1). The values of E calculated

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using Eq. (11) is 1.58–2.5 kJ mol^{-1}, which indicates that the physico-sorption process plays the significant role in the adsorption of MB onto CCS.

Table 1. Comparison of the Coefficients Isotherm Parameters for MB Adsorption onto CCS

Isotherm model	Cucumis Sativa activated carbon concentrations (g /50mL)	
	0.2 (g /50mL)	0.6(g /50mL)
Langmuir		
Q_m (mg g^{-1})	46.730	15.48
K_a (L mg^{-1})	0.1698	0.6715
R^2	0.9645	0.9837
Freundlich		
1/n	0.4299	0.3242
K_F (mg g^{-1})	9.532	6.0464
R^2	0.9897	0.9837
Tempkin		
α (L g^{-1})	3.383	30.78
β (mg L^{-1})	8.0469	2.1599
b	309.96	1154.78
R^2	0.9253	0.9448
Dubinin–Radushkevich		
Q_m (mg g^{-1})	26.36	9.9015
K (×10-5 mol^2 kJ^{-2})	0.01	0.008
E (kJ mol^{-1})	1.581	2.5
R^2	0.9169	0.9006

Kinetic Models Applied to the Adsorption of MB onto CCS

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control, and mass transfer; kinetic models are used to test experimental data from the adsorption of MB onto CCS. The kinetics of MB adsorption onto CCS is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of MB adsorption onto CCS were analyzed using pseudo-

first-order (Lagergren 1898), pseudo-second-order (Ho et al . 2000), Elovich (Chien and Clayton 1980; Sparks 1986; Zeldowitsch 1934), and intraparticle diffusion (Weber et al. 1963; Srinivasan et al. 1988) kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of MB adsorption onto CCS.

Pseudo-first-order equation

The adsorption kinetic data were described by the Lagergren pseudo-first-order model (Lagergren1898), which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{12}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}), and k_1 is the rate constant of pseudo-first-order adsorption (L min^{-1}). Integrating Eq. (12) for the boundary conditions $t = 0$–t and $q_t = 0$–q_t gives

$$\log(\frac{q_e}{q_e - q_t}) = \frac{k_1}{2.303}t \tag{13}$$

Eq. (13) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{14}$$

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t by plotting $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and the predicted q_e value can be determined from the slope and intercept of the plot, respectively (Fig. 4). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Figure 4 shows that the pseudo-first-order equation fit well for the first 50 min and thereafter the data deviated from theory. Thus, the model well represents the initial stages where rapid adsorption occurs but cannot be applied for the entire adsorption process. Furthermore, the correlation coefficients R^2 were relatively low for most adsorption data (Table 2). This shows that the adsorption of MB onto CCS cannot be applied, and the reaction mechanism is not a first-order reaction.

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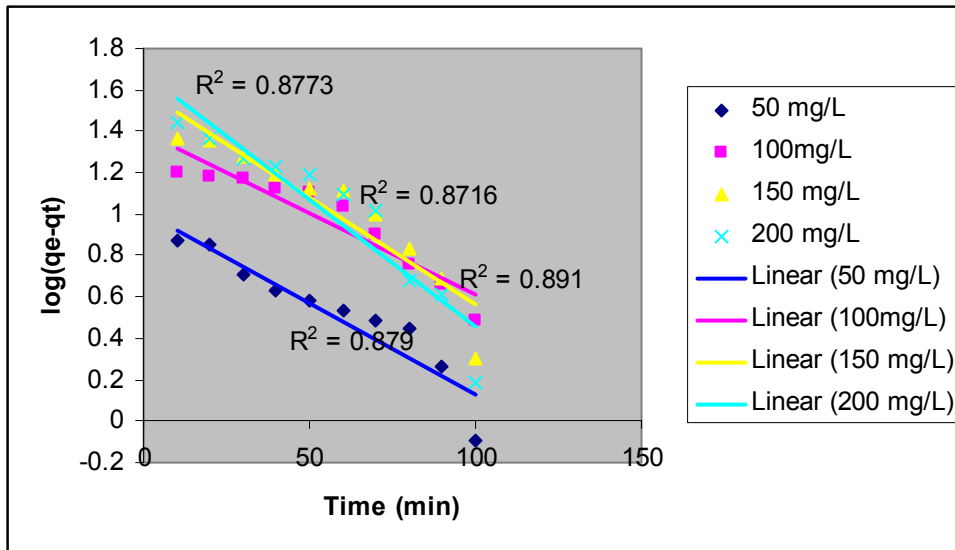
Fig. 4. Pseudo-first-order kinetics for MB adsorption onto CCS. Conditions: adsorbent dosage 0.2 g/50 mL, pH 6.0, temperature 27 ± 2 °C

Pseudo-second-order equation

The adsorption kinetics also may be described by the pseudo-second-order model (Ho et al. 2000). The differential equation is generally given as follows:

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

where k_2 (g (mg min)$^{-1}$) is the second-order rate constant of adsorption. By integrating Eq. (15) for the boundary conditions $q_t = 0–q_t$ at $t = 0–t$, the expression is simplified and can be rearranged and linearized to obtain the following:

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

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = k_2 q_e^2 \tag{17}$$

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t (Fig 5).
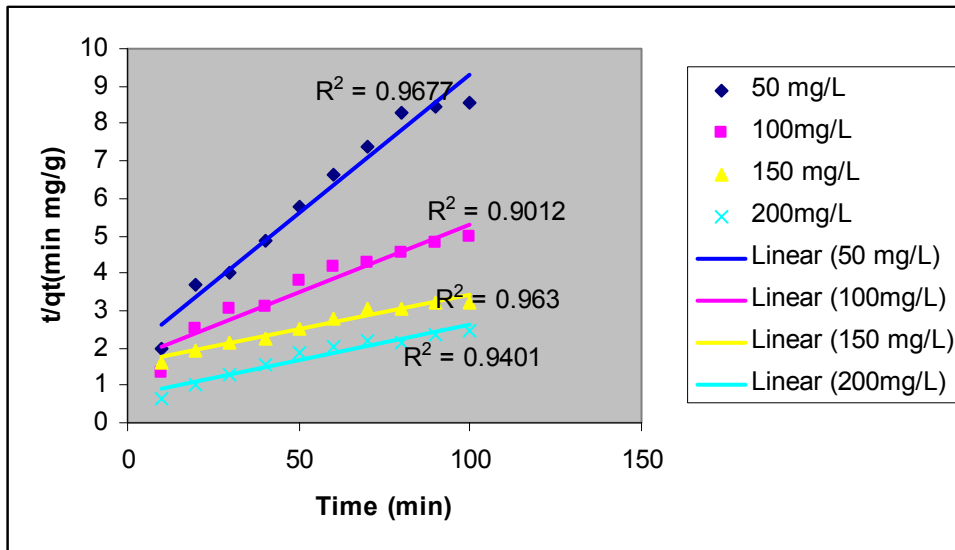
Fig. 5. Plot of the pseudo-second-order model at different initial MB concentrations, CCS 0.2 g /mL, pH 6.0, temperature 27 ± 2 °C

The linear plots of t/q_t versus t showed good agreement between experimental and calculated q_e values at different initial MB and adsorbent concentrations (Table 2). The correlation coefficients for the second-order kinetic model were greater than 0.90, which led us to believe that the pseudo-second-order kinetic model provided a good correlation for the bioadsorption of different initial of MB onto CCS.

The values of initial sorption (h), which represent the rate of initial adsorption, practically increased from 0.5303 to 1.436 mg (g min)$^{-1}$ with the increase in initial MB concentrations from 50 to 200 mg L^{-1} onto CCS dose 0.2 g mL^{-1} (Table 2).

Table 2. Comparison of the First- and Second-Order Adsorption Rate Constants and Calculated and Experimental q_e Values for Different Initial MB and CCS (0.2g /50mL)

Parameter	First-order kinetic model				Second-order kinetic model			
	q_e (experimental)	k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	h	R^2
MB (mg L^{-1})								
50	8.9027	0.02	10.28	0.879	0.003	13.514	0.53	0.968
100	14.603	0.02	24.63	0.891	0.0008	27.47	0.59	0.902
150	22.27	0.02	39.37	0.872	0.872	54.35	0.64	0.963
200	30.19	0.03	47.97	0.877	0.0005	52.36	1.43	0.940

k_1 (min^{-1}), k_2 (g (mg min)$^{-1}$), q_e (mg g^{-1}), h (mg (g min)$^{-1}$).

Elovich equation

The Elovich equation is another rate equation based on the adsorption capacity. It is generally expressed in the following form (Chien and Clayton 1980; Sparks 1986; Zeldowitsch 1934):

$$\frac{dq_t}{dt} = B_E \exp(-A_E q_t) \qquad (18)$$

where B_E is the initial adsorption rate (mg (g min)$^{-1}$) and A_E is the de-sorption constant (g mg^{-1}) during any experiment. This expression can be simplified by assuming $A_E B_E t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Then Eq. (18) becomes:

$$q_t = \frac{1}{A_E} \ln(B_E A_E) + \frac{1}{A_E} \ln(t) \qquad (19)$$

If MB adsorption by CCS fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/A_E)$ and an intercept of $(1/A_E) \ln (A_E B_E)$ (Fig 6). Thus, the constants can be obtained from the slope and the intercept of the straight line (Table 3). The initial adsorption rate B_E increased from 5.88 to 37.03 mg (g min)$^{-1}$ with increase of initial MB concentration from 50 to 200 mg L^{-1} on CCS dose of 0.2 g mL^{-1}. A similar pattern as mentioned above was observed for the initial adsorption rate, h, obtained from pseudo-second-order model. The desorption constant, A_E, decreased from 0.3588 to 0.0900 g mg^{-1} with increase in the initial MB concentration from 50 to 200 mg L^{-1} over CCS dose of 0.2 g mL^{-1} (Table 3).
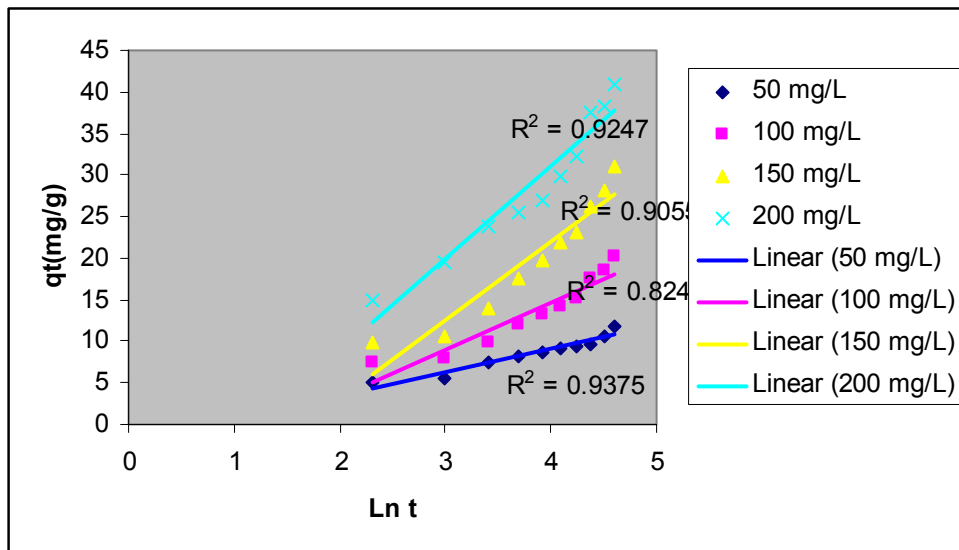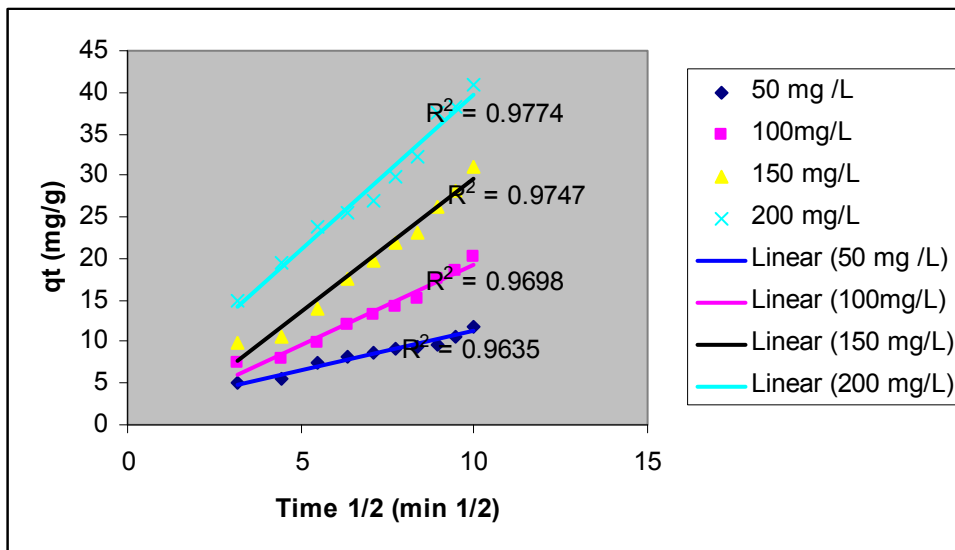

Fig. 6. Elovich model plot for the adsorption of MB onto CCS (0.2g /50mL) at different initial dye concentrations (50, 100 ,150 and 200 mg L^{-1})

The intraparticle diffusion model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through an intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor (McKay 1983). Since the MB molecules are probably transported from its aqueous solution to the CCS by intraparticle diffusion, so the intraparticle diffusion is another kinetic model that should be used to study the rate of MB adsorption onto CCS. The possibility of intraparticular diffusion was explored by using the intraparticle diffusion model, which is commonly expressed by the following equation,

$$q_t = K_{dif}t^{1/2} + C \qquad (20)$$

where C (mg g^{-1}) is the intercept and K_{dif} is the intraparticle diffusion rate constant (in mg g^{-1} min$^{-1/2}$). The values of q_t were found to be linearly correlated with values of $t^{1/2}$ (Fig 7), and the rate constant K_{dif} was directly evaluated from the slope of the regression line (Table 3).

Fig. 7. Intraparticle diffusion model plot for the adsorption of MB onto CCS (0.2 g /50mL) at different initial dye concentration (50, 100, 150, and 200 mg L^{-1})

The values of the intercept C (Table 3) provide information about the thickness of the boundary layer, where the resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase from 0.024 to 2.4415 with increase of dye concentration from 50 to 200 mg L^{-1}, indicating the increase of the thickness of the boundary layer and decrease of the likelihood of the external mass transfer and hence increase of the likelihood of internal mass transfer. The R^2 values given in Table 3 are close to unity, indicating the applicability of this model. This may confirm

that the rate-limiting step is the intraparticle diffusion process. The intraparticle diffusion rate constants, K_{dif}, were in the range of 0.9242 to 3.7338 mg g^{-1} min$^{-1/2}$ and they increased with increasing initial dye concentration. The linearity of the plots demonstrated that intraparticle diffusion played a significant role in the uptake of the adsorbate by adsorbent. However, as still there is no sufficient indication about it, Ho (2003) has shown that if the intraparticle diffusion is the sole rate-limiting step, then it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin, which is not the case in Fig. 7. So it may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the MB and CCS interactions.

Table 3. The Parameters Obtained from Elovich Kinetic Model and Intraparticle Diffusion Model Using Different Initial MB Concentrations

Parameter	Elovich			Intraparticle diffusion		
	A_E	B_E	R^2	K_{dif}	C	R^2
MB (mg L^{-1})						
50	0.36	5.88	0.938	0.92	1.977	0.964
100	0.17	24.89	0.824	1.92	0.024	0.969
150	0.11	50.43	0.906	3.21	2.564	0.975
200	0.09	37.03	0.925	3.73	2.442	0.977

Table 4. Characteristics of CCS

Parameter	Value
pH of 1% solution	6.5
Moisture content(%)	1.62
Water soluble matter(%)	10.12
Acid soluble matter(%)	8.07
Decolorizing power (mg/g)	47.0
Conductivity	0.92
pH$_{ZPC}$	4.0

CONCLUSIONS

1. The results of this investigation show that activated carbon developed from *Cucumis Sativa* has a suitable adsorption capacity for the removal of MB from aqueous solutions.
2. The equilibrium adsorption was practically achieved in 110 min.
3. The experimental results were analyzed by using Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich isotherm models, and the correlation coefficients for

Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich equations were well fitted. Adsorption was well described by a monolayer Langmuir-type isotherm.
4. A kinetic study of MB on CCS was performed based on pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion equations. The data indicate that the adsorption kinetics followed a pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps.
5. CCS can be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of color and dyes from water and wastewater.

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