



Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption

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ABSTRACT

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 epicarp of *Ricinus communis* for the removal of malachite green (MG) 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. Optimum pH value for dye adsorption was 7.0. Maximum dye was sequestered within 50 min of the start of every experiment. The adsorption of malachite green followed the pseudo-second-order rate equation and fits the Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin equations well. The maximum removal of MG was obtained at pH 7 as 99.04% for adsorbent dose of 1 g 50 mL⁻¹ and 25 mg L⁻¹ initial dye concentration at room temperature. Activated carbon developed from *R. communis* can be an attractive option for dye removal from diluted industrial effluents since test reaction made on simulated dyeing wastewater showed better removal percentage of MG.

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1. Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solids [1]. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by their mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons [2,3].

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation [4], adsorption [5], ozonation [6], electrochemical techniques [7], and fungal decolonization [8]. Among these methods adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes [9], but its high cost limits its commercial application. In recent years, there has been growing interest in finding inexpensive and effective alternatives to carbon, such as rice husk [10], chitin [11], orange waste [12], lemon peel

[13], granular kohlrabi peel [14], raw barley straw [15], eggshell [16], silica–zirconia mixed oxide [17], akash kinari coal [18] and TiO₂/AC [19].

Annual production of *Ricinus communis* is estimated to be more than 1.0 tons globally, of which India accounts for 60% of the production. The epicarp of Ricinus is a segregated waste by-product (35% of production) during segregation of *R. communis* seed. Since the epicarp of Ricinus is available free of cost, only the carbonization of its epicarp is involved in the waste water treatment. Therefore the main objective of this study was to evaluate the possibility of using the dried epicarp of Ricinus to develop a new low-cost activated carbon and study its application to remove malachite green (MG) from simulated wastewater. The epicarp of Ricinus was previously investigated to adsorb Crystal violet [20] and Ni (II) [21]. Systematic evaluation of the parameters involved, pH, adsorbent dose, adsorbent particle size, initial dye concentration and time.

2. Materials and methods

2.1. Preparation of activated carbon from epicarp of *R. communis* (CRC)

The epicarp of *R. communis* was obtained from an agricultural farm in Coimbatore district (Tamil Nadu). It was air-dried and powdered in a grinder. It was soaked in concentrated H₂SO₄ for 12 h and

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washed thoroughly with distilled water till 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 $110 \pm 2^\circ\text{C}$. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use.

2.2. Preparation of synthetic solutions

A stock solution of 500 mg L^{-1} was prepared by dissolving the appropriate amount of MG (obtained from S.D. Fine Chemicals, Mumbai, India) in 100 mL and made to 1000 mL with distilled water. Different concentrations ranged between 25 and 200 mg L^{-1} of MG 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 ($27 \pm 2^\circ\text{C}$).

2.3. Batch adsorption studies

2.3.1. Effect of pH on MG adsorption

The effect of pH on the equilibrium uptake of dyes was investigated by employing an initial concentration of MG (100 mg L^{-1}) and $0.2 \text{ g } 50 \text{ mL}^{-1}$ of CRC. The initial pH values were adjusted with 0.1 M HCl or 0.1 M NaOH to form a series of pH from 2 to 10. The suspensions were shaken at room temperature ($27 \pm 2^\circ\text{C}$) using agitation speed (150 rpm), the minimum contact time required to reach the equilibrium (90 min) and the amount of MG adsorbed determined.

2.3.2. Effect of CRC dose on MG adsorption

The effect of adsorbent dose on the equilibrium uptake of MG (100 mg L^{-1}) was investigated with CRC concentrations of 0.2, 0.4, 0.6, 0.8 and $1 \text{ g } 50 \text{ mL}^{-1}$. The experiments were performed by shaking known MG concentration with the above different CRC concentrations to the equilibrium uptake (90 min) and the amount of MG adsorbed was determined.

2.3.3. Kinetics studies

Adsorption studies were conducted in 250-mL shaking flasks at a solution pH of 7.0. CRC ($0.2 \text{ g } 50 \text{ mL}^{-1}$) was thoroughly mixed individually with 50 mL of MG solution ($50, 100, 150$ and 200 mg L^{-1}) 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 and 90 min and were centrifuged for 5 min. The clear solutions were analyzed for residual MG concentration in the solutions.

2.3.4. Adsorption isotherm

Batch adsorption experiments were carried out in a rotary shaker at 150 rpm using 250 mL shaking flasks at room temperature for 90 min. The CRC (0.2, 0.6, and 1 g) was thoroughly mixed with 50 mL of MG solutions. The isotherm studies were performed by varying the initial MG concentrations from 25 to 200 mg L^{-1} at pH 7.0, which was adjusted using 0.1 M HCl or 0.1 M NaOH before addition of CRC and maintained throughout the experiment. After shaking the flasks for 90 min, the reaction mixture was analyzed for the residual MG concentration.

The concentration of MG in solution was measured by using direct UV–vis spectrophotometric method using a Systronic Spectrophotometer-104 at wavelength of 540 nm. All the experiments were duplicated and only the mean values are reported. The maximum deviation observed was less than $\pm 4\%$.

Adsorption of MG from simulated wastewater was studied using $0.2 \text{ g } 50 \text{ mL}^{-1}$ of CRC and MG concentrations 100 mg L^{-1} at initial

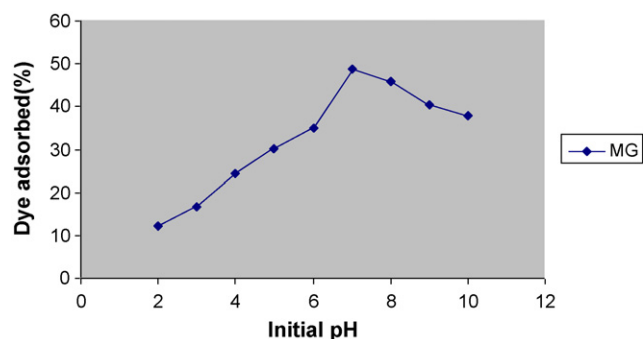


Fig. 1. Effect of system pH on adsorption of MG (100 mg L^{-1}) onto CRC ($0.2 \text{ g } 50 \text{ mL}^{-1}$) at room temperature ($27 \pm 2^\circ\text{C}$), agitation speed 150 rpm for the minimum contact time required to reach the equilibrium (90 min).

pH 7.0. The amount of dye adsorbed at equilibrium onto carbon, q_e (mg g^{-1}), was calculated by the following mass balance relationship:

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

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentration of MG, respectively, V the volume of the solution (L), and W is the weight of the CRC used (g).

3. Results and discussion

3.1. Effect of system pH on MG Uptake

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Fig. 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 MG color is observed at pH 7. Similar trend of pH effect was observed for the adsorption of malachite green on activated carbon prepared from fly ash [22] and tuncbilek lignite [23]. Which may be attributed to the hydrophobic nature of the developed carbon which led to absorb hydrogen ions (H^+) onto the surface of the carbon when immersed in water and made it positively charged. Low pH value (1.0–3.0) leads to an increase in H^+ ion concentration in the system and the surface of the activated carbon acquires positive charge by absorbing H^+ ions. On the other hand, increase of the pH value (7) led to increase of the number of negatively charged sites. As the CRC surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecule leading to maximum adsorption of MG [24] from waste water. The lowest adsorption occurred at pH 2.0 and the highest adsorption occurred at pH ~ 7.0 . Adsorbent surface would be positively charged upto pH < 4 , and heterogeneous in the pH range 4–6. Thereafter, adsorbent surface should be negatively charged. Moreover, the increasing in the adsorption of MG with increasing of pH value is also due to the attraction between cationic dye and excess OH^- ions in the solution.

3.2. Effect of contact time and initial MG concentration

The relation between removal of MG and reaction time were studied to see the rate of dye removal. The results of percentage removal of MG at pH 7.0 with increase of contact time using CRC, the results are presented in Fig. 2. It was found that more than 50% removal of MG concentration occurred in the first 10 min, and

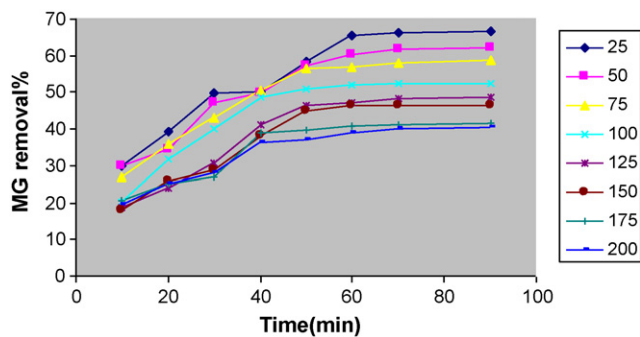


Fig. 2. Effect of contact time on the removal of different initial concentrations of MG using CRC (0.2 g 50 mL⁻¹) at pH 7.0.

thereafter the rate of adsorption of the MG onto CRC was found to be slow. The rapid adsorption at the initial contact time is due to the highly negatively charged surface of the CRC for adsorption of cationic MG in the solution at pH 7. Later slow rate of MG adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species onto the surface of CRC 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 90 min when the maximum MG adsorption onto CRC was reached.

Also, the effect of initial concentration of MG in the solution on the capacity of adsorption onto CRC was studied and is shown in Fig. 2. The experiments were carried out at fixed adsorbent dose (0.2 g 50 mL⁻¹) in the test solution at room temperature (27 ± 2 °C), pH 7 and at different initial concentrations of MG (25, 50, 75, 100, 125, 150, 175 and 200 mg L⁻¹) for different time intervals (10, 20, 30, 40, 50, 60, 70, 80 and 90 min). Fig. 2 shows that the percentage of adsorption efficiency of CRC decreased with the increase of initial MG concentration in the solution. Though the percent adsorption decreased with increase in initial dye concentration, the actual amount of MG adsorbed per unit mass of adsorbent increased with increase in MG concentration in the test solution.

It is evident from Fig. 2 that the amount adsorbed on CRC at a lower initial concentration of MG was smaller than the corresponding amount when higher initial concentrations were used. However, the percentage removal of MG was greater at lower initial concentrations and smaller at higher initial concentrations. The adsorption capacity for CRC was increased from 4.17 to 20.18 mg g⁻¹ as the MG concentration increased from 25 to 200 mg L⁻¹. In the process of MG adsorption initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time.

3.3. Effect of adsorbent mass on MG adsorption

The adsorption of MG on CRC was studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g 50 mL⁻¹) in the test solution while keeping the initial MG concentration (100 mg L⁻¹), temperature (27 ± 2 °C) and pH (7.0) constant at contact times for 90 min (Fig. 3). The adsorption increased from 48.65% to 76.92%, as the CRC dose increased from 0.2 g to 1.0 g 50 mL⁻¹ at equilibrium time (90 min). Maximum MG removal was achieved within 10–50 min after which MG concentration in the reaction solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to increased MG surface area and availability of more adsorption sites, while the unit adsorbed of MG decreased with increase in CRC dose.

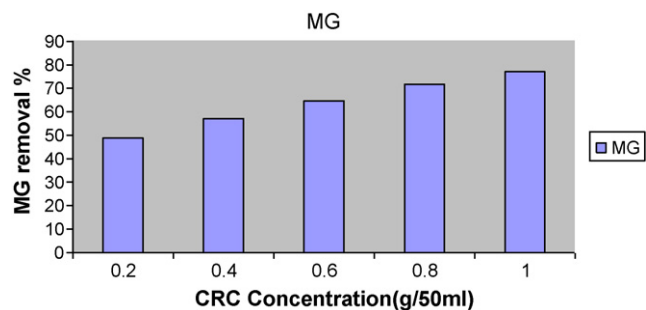


Fig. 3. Effect of adsorbent concentration on MG removals (C_0 : 100 mg L⁻¹, pH 7.0, agitation speed: 150 rpm, temperature: 27 ± 2 °C).

3.4. 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.

3.4.1. Langmuir isotherm

The theoretical Langmuir isotherm [25] 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 [26]. 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 nonlinear equation is commonly expressed as followed:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

In Eq. (2), C_e and q_e are as defined before in Eq. (1), Q_m is a constant and reflect 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 [27,28].

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \quad (3)$$

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 MG onto CRC are shown in Table 1. The correlation coefficients reported in Table 1 showed strong positive evidence on the adsorption of MG onto CRC follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to CRC was proved by the high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the sorption

Table 1
Comparison of the coefficients isotherm parameters for MG adsorption onto CRC.

Isotherm model	Ricinus communis activated carbon concentrations (g 50 mL ⁻¹)		
	0.2	0.6	1
Langmuir			
Q_m (mg g ⁻¹)	5.3305	10.753	27.78
K_a (L mg ⁻¹)	4.096	0.0417	0.0203
R^2	0.987	0.984	0.993
Freundlich			
$1/n$	0.578	0.5452	0.2613
K_F (mg g ⁻¹)	1.357	1.189	2.3046
R^2	0.982	0.927	0.906
Tempkin			
α (L g ⁻¹)	0.0012	2.071	10.71
β (mg L ⁻¹)	9.8921	2.4501	0.9288
b	252.14	1017.99	2685.4
R^2	0.9034	0.9709	0.9431
Dubinin–Radushkevich			
Q_m (mg g ⁻¹)	16.33	7.349	5.263
K ($\times 10^{-5}$ mol ² kJ ⁻²)	2.00	4.00	0.008
E (kJ mol ⁻¹)	0.158	0.1118	2.500
R^2	0.9201	0.9455	0.9404

system. The maximum monolayer capacity Q_m obtained from the Langmuir is 27.78 mg g⁻¹.

3.4.2. The Freundlich isotherm

The Freundlich isotherm model [29] is the earliest known equation 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:

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

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. Eq. (4) can be linearized in the logarithmic form (Eq. (5)) and the Freundlich constants can be determined:

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

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 MG onto CRC 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 MG is favorably adsorbed by CRC.

3.4.3. The Tempkin isotherm

Tempkin adsorption isotherm model was used to evaluate the adsorption potentials of the CRC for MG. 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 [30–32]:

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

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

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (7)$$

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 [33,34]. The adsorption data were analyzed according to the linear form of the Tempkin isotherm Eq. (7). Examination of the data shows that the Tempkin isotherm fitted well the MG adsorption data for CRC. The linear isotherm constants and coefficients of determination are presented in Table 1. The heat of MG adsorption onto CRC was found to increase from 0.252 to 2.685 kJ mol⁻¹ with increase of CRC dose from 0.2 to 1.0 g L⁻¹. The correlation coefficients R^2 obtained from Tempkin model were comparable to that obtained for Langmuir and Freundlich equations, which explain the applicability of Tempkin model to the adsorption of MG onto CRC.

3.4.4. 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 [35–37]. The D–R isotherm does not assume 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):

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (8)$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (9)$$

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

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

The slope of the plot of $\ln q_e$ versus ε^2 gives K (mol²(kJ²)⁻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 [38]:

$$E = \frac{1}{\sqrt{2K}} \quad (11)$$

The calculated value of D–R parameters is given in Table 1. The saturation adsorption capacity Q_m obtained using D–R isotherm model for adsorption of MG onto CRC is 16.33 mg g^{-1} at $0.2 \text{ g } 50 \text{ mL}^{-1}$ adsorbent dose, which is close to that obtained (10.753 mg g^{-1}) from Langmuir isotherm model (Table 1). The values of E calculated using Eq. (11) is $0.158\text{--}2.500 \text{ kJ mol}^{-1}$, which indicating that the physico-sorption process plays the significant role in the adsorption of MG onto CRC.

3.5. Kinetic models applied to the adsorption of MG onto CRC

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 MG onto CRC. The kinetics of MG adsorption onto CRC 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 MG adsorption onto CRC were analyzed using pseudo-first-order [39], pseudo-second-order [40], Elovich [41–43] and intraparticle diffusion [44,45] 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 MG adsorption onto CRC.

3.5.1. Pseudo-first-order equation

The adsorption kinetic data were described by the Lagergren pseudo-first-order model [39], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expresses a follows:

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

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively, (mg g^{-1}), 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

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

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

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

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t by plot of $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and predicted q_e 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. Fig. 4 shows that the pseudo-first-order equation fits well for the first 50 min and thereafter the data deviate from theory. Thus, the

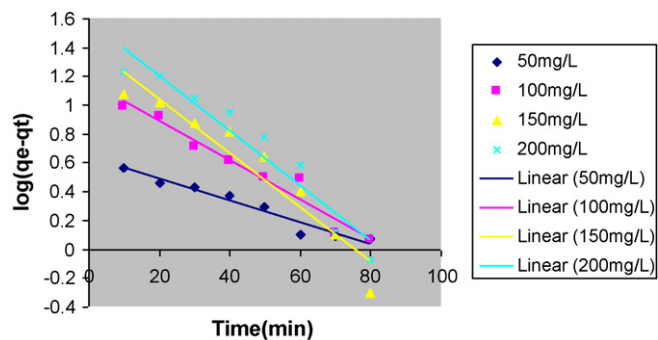


Fig. 4. Pseudo-first-order kinetics for MG adsorption onto CRC. Conditions: adsorbent dosage $0.2 \text{ g } 50 \text{ mL}^{-1}$, pH 7.0, temperature $27 \pm 2^\circ \text{C}$.

model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the correlation coefficient R^2 are relatively low for most adsorption data (Table 2). This shows that the adsorption of MG onto CRC cannot be applied and the reaction mechanism is not a first-order reaction.

3.5.2. Pseudo-second-order equation

The adsorption kinetic may be described by the pseudo-second-order model [40]. The differential equation is generally given as follows:

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

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

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

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

$$h = k_2 q_e^2 \quad (17)$$

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). The linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at different initial MG and adsorbent concentrations (Table 2). The correlation coefficients for the second-order kinetic model are greater than 0.95, which led to believe that the pseudo-second-order kinetic model provided good correlation for the bioadsorption of different initial of MG onto CRC.

The values of initial sorption (h) that represents the rate of initial adsorption, is practically increased from 0.1348 to $1.865 \text{ mg}(\text{g min})^{-1}$ with the increase in initial MG concentrations from 50 to 200 mg L^{-1} onto CRC dose 0.2 g mL^{-1} (Table 2). It was observed that the pseudo-second-order rate constant (k_2)

Table 2

Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial MG and CRC ($0.2 \text{ g } 50 \text{ mL}^{-1}$).

Parameter			First-order kinetic model			Second-order kinetic model				
	CRC concentration ($\text{g } 50 \text{ mL}^{-1}$)	MG (mg L^{-1})	q_e (experimental)	k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	h	R^2
0.2		50	4.875	0.02	4.354	0.952	0.004	5.64	0.14	0.946
		100	13.16	0.03	14.54	0.958	0.003	14.56	0.73	0.960
		150	22.50	0.04	26.62	0.919	0.002	27.70	1.17	0.973
		200	34.00	0.04	39.14	0.926	0.001	41.66	1.87	0.973

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

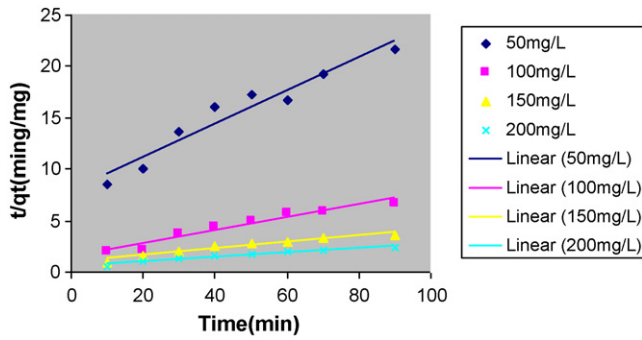


Fig. 5. Plot of the pseudo-second-order model at different initial MG concentrations, CRC 0.2 g mL⁻¹, pH 7.0, temperature 27 ± 2 °C.

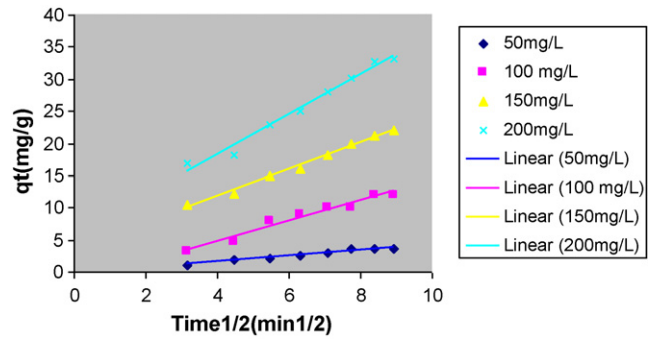


Fig. 7. Intraparticle diffusion model plot for the adsorption of MG onto CRC (0.2 g 50 mL⁻¹) at different initial dye concentration (50, 100, 150 and 200 mg L⁻¹).

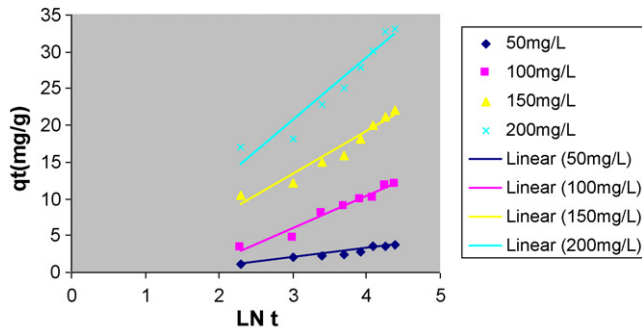


Fig. 6. Elovich model plot for the adsorption of MG onto CRC (0.2 g 50 mL⁻¹) at different initial dye concentrations (50, 100, 150 and 200 mg L⁻¹).

decreased from 0.004239 to 0.00107 with increased initial MG concentration from 50 to 200 mg L⁻¹ for CRC dose of 0.2 g mL⁻¹.

3.5.3. Elovich equation

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as following [41–43]:

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

where B_E is the initial adsorption rate (mg(g min)⁻¹) and A_E is the desorption constant (g mg⁻¹) during any experiment.

It is simplified by assuming $A_E B_E t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (18) becomes:

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

If MG adsorption by CRC 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 increase from 5.53 to 832.52 mg(g min)⁻¹ with increase of initial MG concentration from 50 to 200 mg L⁻¹ on CRC dose of 0.2 g mL⁻¹. Similar pattern is mentioned above for the initial adsorption rate, h , obtained from pseudo-second-order model. The desorption constant, A_E , decrease

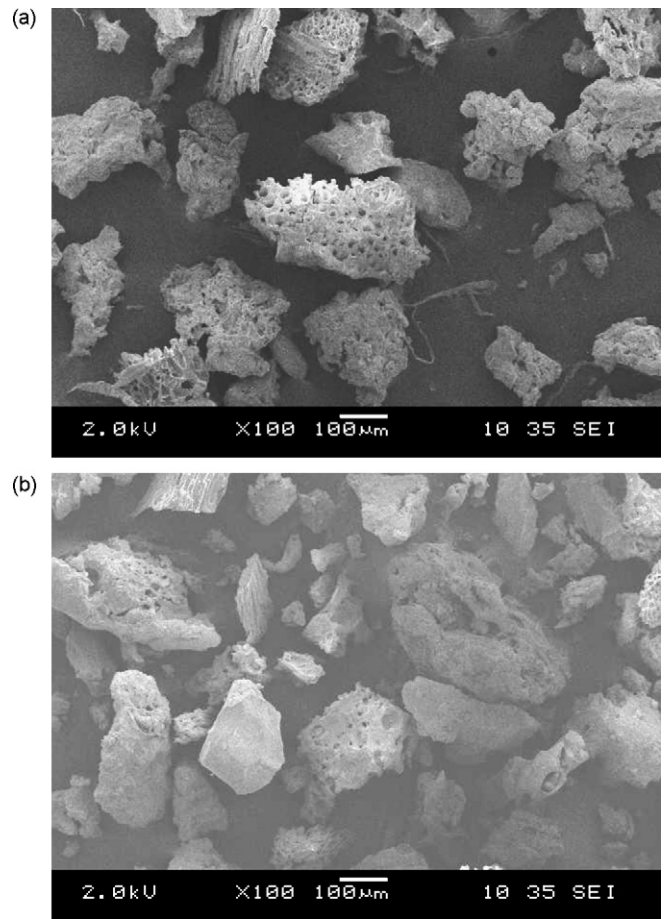


Fig. 8. (a) SEM photograph for CRC (Before adsorption) (b) SEM photograph for CRC (After adsorption).

from 0.7933 to 0.1169 g mg⁻¹ with increase in the initial MG concentration from 50 to 200 mg L⁻¹ over CRC dose of 0.2 g mL⁻¹ (Table 3).

Table 3

The parameters obtained from Elovich kinetics model and intraparticle diffusion model using different initial MG concentrations.

CRC concentration (g 50 mL ⁻¹)	MG concentration (mg L ⁻¹)	Elovich			Intraparticle diffusion		
		A_E	B_E	R^2	K_{dif}	C	R^2
0.02	50	0.79	5.5	0.948	0.45	0.193	0.967
	100	0.45	11.03	0.977	1.57	1.473	0.964
	150	0.17	12.03	0.948	2.11	3.33	0.988
	200	0.12	15.65	0.935	3.09	5.89	0.979

of the data on MG sorption capacity (values of Q_m derived from the Langmuir equation) of various adsorbents, especially the low-cost adsorbents, is summarized in Table 4. In the present study, the experimental values were used in Langmuir equation to describe the isothermal sorption data. It was found that *R. communis* is an excellent adsorbent for MG.

3.7. Spectrochemical characterization

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM) the results are shown in (Fig. 8a and b). From the SEM analysis, it was found that there were holes and cave type openings on the surface of the adsorbent, which would have more surface area available for adsorption [53]. However, following dye adsorption, the particle surface becomes much smoother than that of the original particle. It is evident that the surface morphology of the activated carbon is different before and after adsorption.

The FT-IR spectrum of the activated carbon (Fig. 9) showed that the most prominent peaks in the spectrum originate from OH vibrations, CH_2 and CH_3 asymmetric and symmetric stretching vibrations. The peaks at ($1155\text{--}1033\text{ cm}^{-1}$) region related to lignin. Therefore, it is possible that cellulose, hemicellulose as well as lignin, having many OH groups in their structure, make up most of the absorbing layer. Two strong peaks observed in the range between 2963 cm^{-1} and 2853 cm^{-1} are assigned to asymmetric C–H bands and symmetric C–H bands, respectively, present in methyl and methylene groups. Stretching vibration band around 1700 cm^{-1} is assigned to carbonyl C=O group present in aldehyde, ester, ketone and acetyl derivatives. The strong band at 1600 cm^{-1} may be due to C=C band. These specific functional groups enhance the adsorption properties [54].

4. Conclusion

The results of this investigation show that activated carbon developed from *R. communis* has a suitable adsorption capacity for the removal of MG from aqueous solutions. The equilibrium adsorption is practically achieved in 90 min. 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 are well fitted. Adsorption behavior is described by a monolayer Langmuir-type isotherm. The kinetic study of MG on CRC was performed based on pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps. The present study concludes that the CRC could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of color and dyes from water and wastewater. *R. communis* has a widespread geographical distribution and is a rapid growing plant that can significantly increase biomass and has little economic value and excellent adsorption capacity for MG, *R. communis* should be a promising and cost-effective adsorbent for MG removal in industry. Further studies on quantitative characterization of this adsorbent and involved mechanisms, and feasibility of using this adsorbent for other triphenylmethane dyes and for its possible industrial application are needed.

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