

Research Article

# Equilibrium and kinetic study for the removal of malachite green using activated carbon prepared from *Borassus flabellofer* male flower

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**ABSTRACT:** Activated carbon was prepared from dried *Borassus flabellofer* male flower and batch adsorption experiments were conducted to study its potential to remove malachite green (MG) dye. The process was further optimized by studying the operating variables like initial pH of the stock solution, activation temperature, initial dye concentration, adsorbent loading and contact time. The optimized pH and activation temperatures were found to be 7.55 and 450 °C respectively, where further analysis was made using these optimal variables. Linear, Freundlich and Langmuir isotherms were studied and it was found that the Langmuir isotherms have the highest correlation coefficients compared to the others. Further, the sorption kinetics were analysed using pseudo-first-order and pseudo-second-order kinetic models. The data showed that the second-order equation was the more appropriate, which indicate that the intra-particle diffusion is the rate limiting factor. © 2009 Curtin University of Technology and John Wiley & Sons, Ltd.

**KEYWORDS:** *Borassus flabellofer* male flower; malachite green; activated carbon; equilibrium; kinetics

## INTRODUCTION

The dyeing industry is one of the largest industries in the world which incorporates textile, leather, cosmetics, paper, printing, plastics, pharmaceutical and fast food industries. These are the major pollutant-causing industries in the world. Presently, more than 9000 dyes are in the colour index belonging to various chemical application classes. Among these dyes, textile industries alone use two-thirds of the total dye products, and about 15–20% of the dyes come from textile effluents<sup>[1]</sup>. Among many contaminants present in wastewater such as, acids, bases, colours, toxic organic and inorganic dissolved solids, colours are considered the most undesirable contaminant, which are mainly caused by the dyes<sup>[2,3]</sup>. Dyes may significantly affect photosynthetic activity in aquatic life because of reduced light penetration, and may also be toxic to some aquatic life due to the presence of aromatics and metals, chlorides, etc. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade<sup>[4,5]</sup>. Removal of

colour from dye-bearing wastewater is a complex problem because of difficulty in treating such wastewaters by conventional treatment methods<sup>[6]</sup>.

Over 90% of some 4000 dyes tested in an Ecological and Toxicological Association of the dyestuff (ETDA) survey had LD<sub>50</sub> values greater than 200 mg/kg. The highest rates of toxicity were found amongst basic and diazo direct dyes<sup>[7,8]</sup>. Recently, the Minimum National Standards (MINAS) have been developed for different industries by Central Pollution Control Board, New Delhi (India). Accordingly, industries have been required to reduce the pollution load, including decolourization, of their effluents before disposal into surface waters, municipal sewage systems or on land.

Dye-contaminated industrial waste water can be treated by physical or chemical or biological methods. These include flocculation, electro-floatation, ion exchange, membrane filtration, precipitation, electrochemical destruction, electro-kinetic coagulation, ozonation, and microbial action<sup>[9]</sup>, where these processes are costly and cannot be used effectively for a wide range of dyestuffs. Surface adsorption method is found to be a superior technique for dye removal in terms of initial cost, easy operation, more regeneration cycle, and inhibition to toxicology. For surface adsorption, activated carbon is the best choice when compared

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with the other natural adsorbent, because of its higher surface area, well defined micropore structure and high adsorption capacity<sup>[10]</sup>. Activated carbon can be used either as granules or in powdered form. But the commercial activated carbon produced from wood and other raw material are costly. This has led to the search for cheaper substitutes. Though several cheap sources are activated and investigated for their adsorption capacity, which includes banana pith, waste coir pith, bagasse pith, rice husk, saw dust, etc. more new economical, easily available and effective adsorption materials are needed.

*Borassus Flabellifer* is a semi-tropical plant commonly found in all parts of India. It is commonly called Palmyra palm, toddy or wine palm, siwalan, rontal, lontar and talauniksha palm in different parts of the world. This semi-tropical plant is found in major parts of all tropical countries like India, Sri Lanka, Southeast Asia, New Guinea, etc. It has both a male and female tree, where the female tree produces palm fruits and male tree produces only the flowers. These semi-hardwood type flowers are not utilized in any form, where in core these are collected and used as domestic fuel in some places. Utilizing these types of natural sources for the production of activated carbon and further using this activated carbon for the removal of malachite green (MG) dye from the effluents, will be a most economical process.

MG is a triphenyl methane dye, which is most widely used for colouring purposes, amongst all other dyes of its category<sup>[11]</sup>. MG has properties that make it difficult to remove from aqueous solutions. If a solution containing MG is discharged into receiving streams, it will affect the aquatic life and cause detrimental effects to the liver, gill, kidney, intestine and gonads. In humans, it may cause irritation to the gastrointestinal tract upon ingestion. Contact of MG with skin causes irritation and redness and pain. Upon contact with eye it will lead to permanent injury of the eye and laboratory animals<sup>[12]</sup>. In this study, it is aimed to evaluate the adsorption capacity of activated carbon of the palm male flower by analysing the activation temperature, sorbent loading, contact time, initial pH and initial concentration of MG dye solution. Further equilibrium and kinetic studies were conducted to understand sorption process and optimization of the above mentioned parameters for maximum dry removal.

## MATERIALS AND METHODS

### Preparation Of adsorbent

In this study, the *Borassus flabellifer* male flower, which is commonly called palm male flower (PMF), was used to produce activated carbon. The PMF has a cylindrical shape of about 30 cm long, and is 2–3 cm dia. The photographic view of PMF is shown in the

Fig. 1. Palm male flowers were collected and sun dried and ground into small particles. It is then sieved to have a uniform particle size. Uniform PMF particles were carbonized in a muffle furnace (300 °C–500 °C) using a china crucible container. The resulting carbon was washed in distilled water to remove traces of ash and then dried in open sunlight. The dried activated carbon was ground well to a fine powder and then stored in an airtight container for further analysis. The shape and structure of the pore on the surface of the PMF-activated carbon were observed using SEM image analysis which is shown in the Figs 2–5.

### Dye solution

MG dye is widely used in textile, paper and carpet industries. MG dye (C<sub>23</sub>H<sub>26</sub>ON<sub>2</sub>, nature = basic green,



Figure 1. Picture of *Borassus flabellifer* male flower.

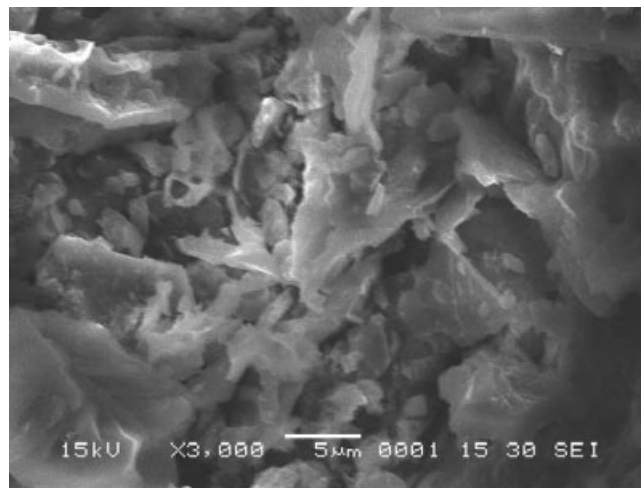
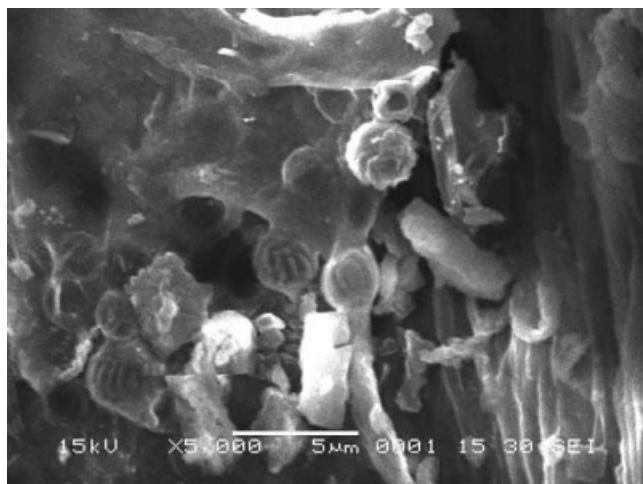
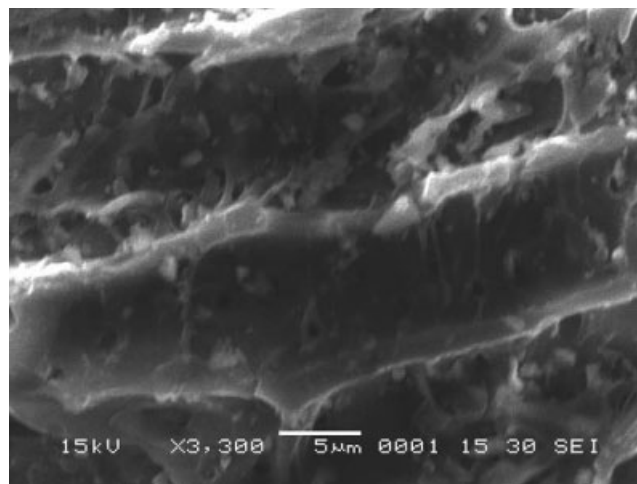


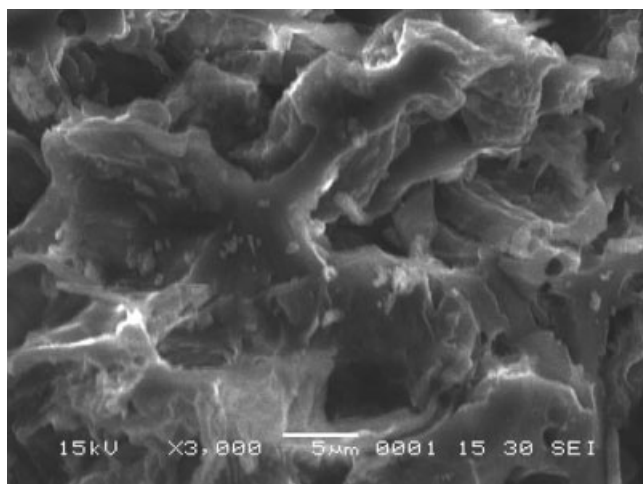
Figure 2. SEM of *Borassus flabellifer* male flower activated at 350 °C at 3000×.



**Figure 3.** SEM of *Borassus flabellofer* male flower activated at 350 °C at 5000 $\times$ .



**Figure 5.** SEM of *Borassus flabellofer* male flower activated at 450 °C at 3300 $\times$ .

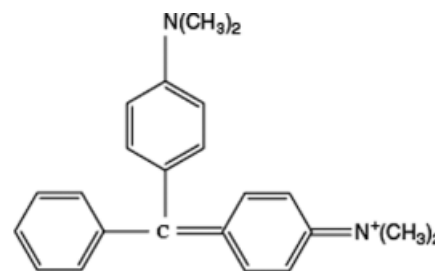


**Figure 4.** SEM of *Borassus flabellofer* male flower activated at 450 °C at 3000 $\times$ .

mp = 112–114 °C and  $\lambda$  max = 617 nm (reported) was supplied by S.D. Fine Chemicals, Mumbai, India. The structure of MG is shown in Fig. 6. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (1000 mg/l). Experimental solutions of the desired concentration were obtained by successive dilutions of stock solution.

## Method

For each adsorption cycle, 20 ml of known concentration of dye solution was prepared from stock solution and 0.025 g of activated carbon was added in a 250 ml conical flask. The mixture was stirred in a temperature-controlled orbital shaker at 120 rpm for a preset interval. At the end of the experiment the adsorbent was separated using high-speed centrifuge operated at 5000 rpm



**Figure 6.** Structure of Malachite Green.

for 10 min. The supernatant was separated and the dye concentration was determined at 617 nm (using a spectrophotometer) in a silica cell having a path length of 1cm where distilled water was used as a blank solution. Further, the experiments were conducted at various initial pH ranging from 4 to 9. The initial pH of the solution was altered by using 0.1N HCl and 0.1N NaOH solutions, where the pH was measured using a digital pH meter.

## Equilibrium study

The equilibrium studies were carried out using 0.025 g of activated carbon in 20 ml MG solution of different concentration. The optimal pH value was maintained using 0.1N HCl solution. The sorption capacity of powdered activated carbon was evaluated by the amount of dye sorbed:  $q = (C_0 - C) \cdot V \cdot 10^{-3} / G$ , (mg of dye/g of sorbent) and by percent of dye removal:  $R\% = (C_0 - C) \cdot 100 / C_0$ , where  $C_0$  and  $C$  are initial and the equilibrium concentration of dye in solution (mg/l),  $G$  is amount of sorbent (g) and  $V$  is volume of solution (ml).

## Kinetic study

Effect of contact time was determined by the 'limited bath' technique. A 0.3125 g of palm male flower activated carbon was added to a known volume (250 ml) of MG dye solution. The initial dye concentration was fixed as 60 mg/l. The temperature of the solution was held constant at 25 °C with a temperature control stirrer. At different time intervals (from 15 min to 5 h), volumes of 1 ml supernatant were taken for spectrophotometric measurements of dye content. The extent of sorption was expressed by the fractional attainment of equilibrium,  $F = q_t/q$  where,  $q_t$  and  $q$  are the amounts of sorbed dye per gram of resin at time  $t$  and after reaching equilibrium respectively (5 h).

## RESULT AND DISCUSSION

The activated carbon prepared from the *Borassus flabellifer* male flower is directly used to remove MG dye using batch process. The effect of pH, initial dye concentration, activated carbon loading, and activation temperature were experimentally studied in detail and the results were analysed as follows. Further different isotherms and kinetic studies were analysed and the complete process was optimized.

### Effect of pH

The effect of initial pH of the dye solution is shown in the Fig. 7. The sorption of MG on activated carbon has a significant variation with the change in the pH. The original dye solution has a pH of 6.89. From the figure it was observed that, by increasing the pH of the dye solution, the percentage adsorption was increased. PMF-activated carbon has maximum adsorption (94.67%) when the pH was increased to 7.55, where the adsorption decreased to 93.39% when the pH was further increased to 9. In the lower range of pH between 2 and 6.89, the adsorption capacity was minimum when compared to a higher pH range. At lower pH the  $H^+$  ions present in the dye solution compete with the dye cations, which reduce the adsorption efficiency<sup>[13]</sup>. At higher pH, the surface of the adsorbent gets negatively charged, which enhance the adsorption process through electrostatic force of attraction.

### Effect of activation temperature

Palm male flower was activated at different temperatures starting from 100 °C to 500 °C. At lower temperatures, i.e. 100–250 °C, the activation was not achieved,

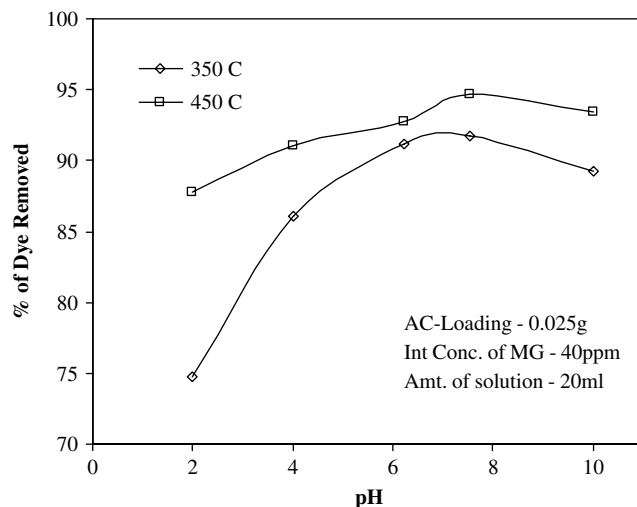


Figure 7. Effect of initial pH of dye solution on % of dye removal.

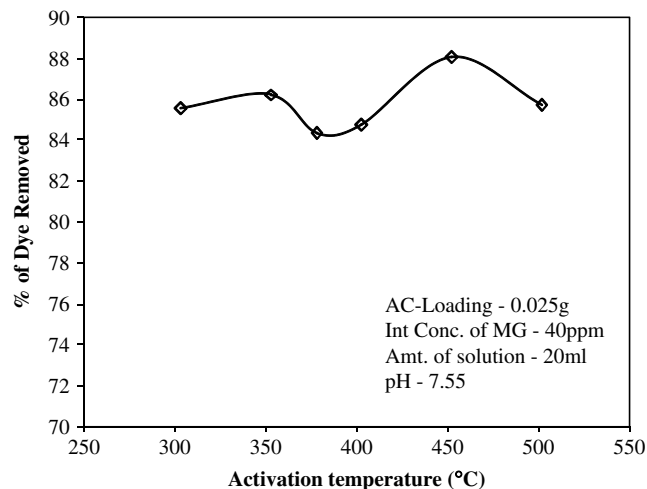
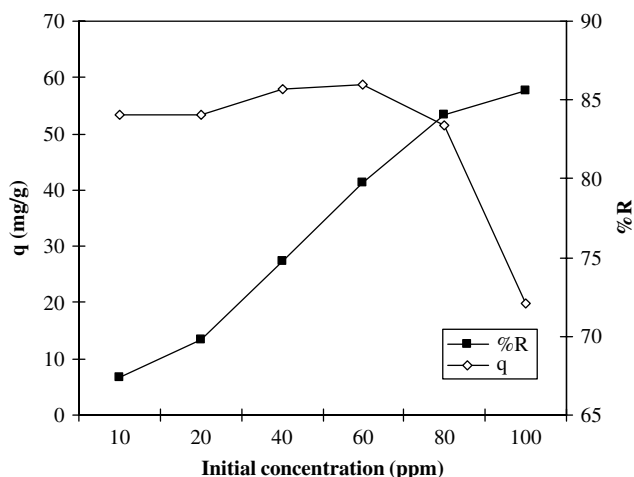


Figure 8. Effect of activation temperature on % of dye removal.

and a further increase in the temperature produced good quality of activated carbon, which was conformed visually based on its surface shininess and its ash content. But at higher activation temperature of about 500 °C the carbon gets charred and loses its basic surface properties. The experiments were carried out at an initial dye concentration of 40 mg/l and 0.025 g of activated carbon with an optimized pH of 7.55 in a temperature-controlled orbital shaker for a preset interval. Fig. 8 shows the adsorption efficiency of the activated carbon produced at different temperatures. From the figure it was observed that the carbon produced at 450 °C has maximum adsorption capacity, and also carbon produced at 350 °C has a maximum adsorption capacity next to 450 °C activation.



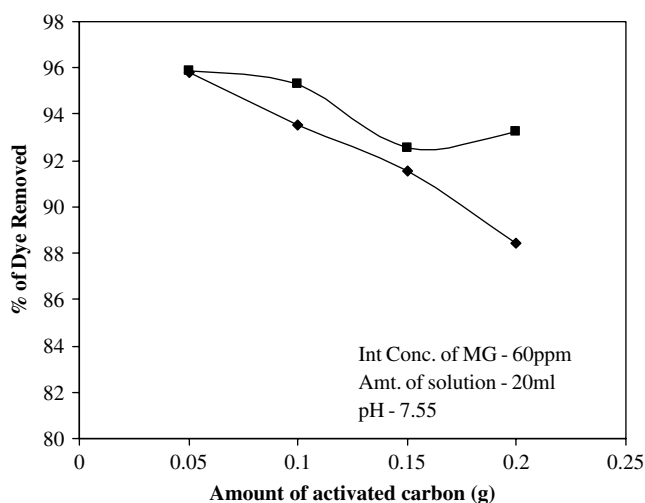
**Figure 9.** The influence of initial dye concentration on the sorption of the dye on activated charcoal ( $T = 25^\circ\text{C}$ ).

### Effect of initial dye concentration

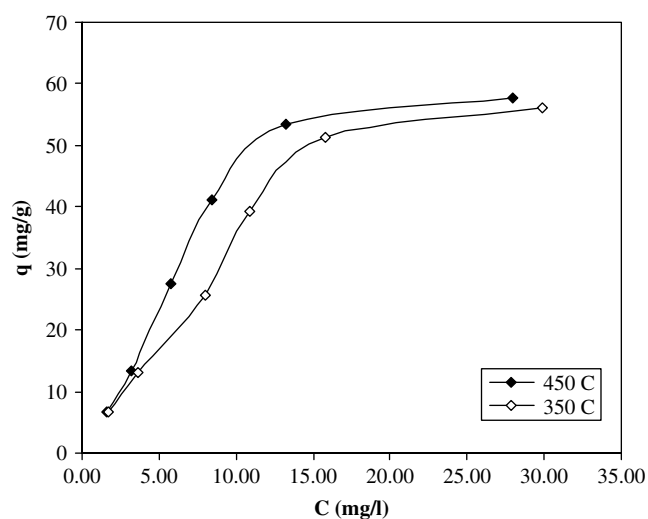
The sorption capacity of powdered PMF-activated carbon for MG was studied at different initial dye concentration. The experiments were carried out at a fixed adsorption dosage of 0.025 g/20 ml at room temperature with optimized pH at different initial concentration of MG (10, 20, 40, 60, 80 and 100 mg/l). From Fig. 9 it was observed that the amount of dye sorbed increases as initial dye concentration increases, whereas the percentage of dye removed (%R) decreased as the initial concentration increased. The curve shows an exponential relation between the initial concentration and the amount of dye adsorbed which accord well with the findings of other investigators<sup>[14]</sup>.

### Effect of adsorbent dosage

Further, the adsorption of MG on PMF-activated carbon was studied by changing the quantity of adsorbent (0.05, 0.1, 0.15, 0.2 and 0.25 g/20 ml) in the test solution while keeping the initial dye concentration as 40 and 60 mg/l at room temperature and at optimized pH for a known time interval. From the analysis, it was observed that the amount of dye sorbed decreased with increasing adsorbent dosage (Fig. 10). Maximum dye removal was achieved with 0.05 mg at its equilibrium time. Decrease in the percentage removal of dye (%R) with adsorbent dose can be attributed to decrease in the adsorbent surface area and availability of more adsorption sites. This may be attributed due to the overlapping or aggregation of adsorbent resulting in decrease in the total adsorbent surface area available to MG, and an increase in diffusion path length.



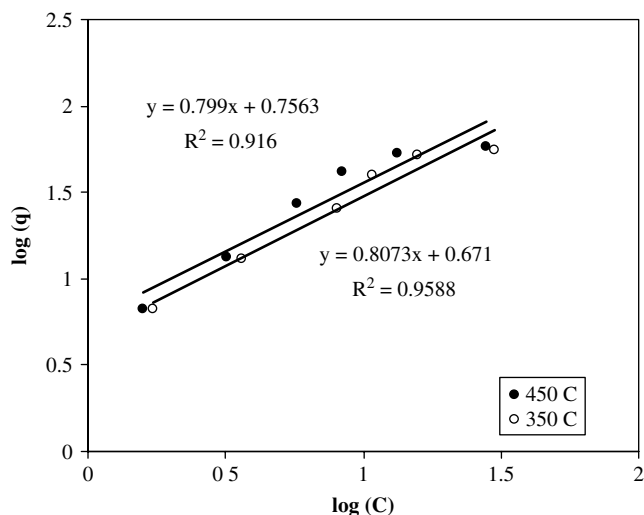
**Figure 10.** Effect of adsorbent dosage on the % of dye removal.



**Figure 11.** The sorption isotherms of the basic dye on activated charcoal at two activation temperatures.

### Sorption isotherm

The equilibrium relationship between the concentration of the adsorbate on the solid phase and in the liquid phase is isotherm. The sorption isotherms of the basic MG dye on activated carbon of the palm male flower at room temperatures are represented in Fig. 11. The experimental equilibrium sorption data were analysed using three adsorption isotherm models (Eqns 1–3): the linear<sup>[15]</sup>, the Freundlich<sup>[16]</sup> and the Langmuir<sup>[17]</sup> expressed by Eqns 1–3, where  $K_F$  parameter is relative to the adsorption capacity and  $n$  is a measure of sorption intensity; favourable sorption correspond to a value of  $1 < n < 10$ . For  $n = 1$ ,  $K_F = K$  (linear isotherm). The Langmuir constant,  $K_L$  is related to energy of the sorption and  $q_0$  is the maximum value of



**Figure 12.** Freundlich plots for the sorption of the basic dye on activated carbon.

sorption capacity (corresponding to complete monolayer coverage).

$$\text{Linear Isotherm : } q = K \cdot C \quad (1)$$

$$\text{Freundlich Isotherm : } q = K_F \cdot C^{1/n} \quad (2)$$

$$\text{Langmuir Isotherm : } q = \frac{(K_L \cdot C \cdot q_0)}{(1 + K_L \cdot C)} \quad (3)$$

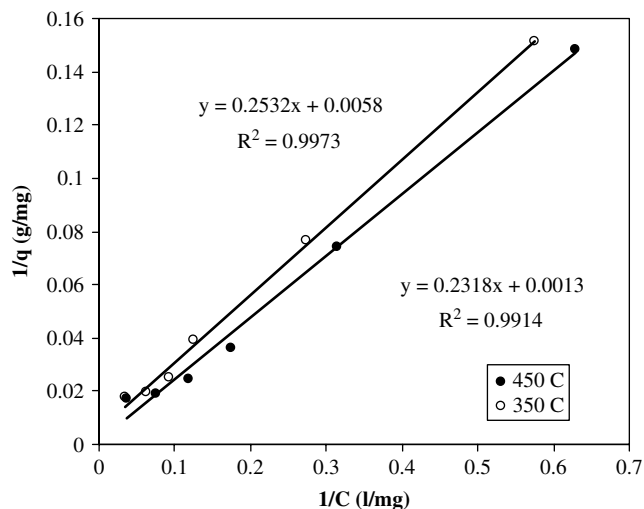
In the above isotherms the Freundlich isotherm and Langmuir isotherm parameters were determined by suitably converting the corresponding equation in its linear form as shown below.

$$\text{Log } q = \text{log } K_F + 1/n \text{ log } C \quad (4)$$

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L + q_0} \cdot \frac{1}{c} \quad (5)$$

Fig. 12 shows the Freundlich isotherm model and Fig. 13 shows the Langmuir isotherm model for the equilibrium data of MG and PMF-activated carbon.

The slope and intercept of the above equations were used to calculate the binding parameters of the system ( $K_F$ ,  $K_L$  and  $n$ ). The  $K_F$ ,  $K_L$  and  $n$  values are listed in Table 1 along with the correlation coefficient  $R^2$  which shows the overall deviation of the experimental points. From the table it was observed that



**Figure 13.** Langmuir plots for the sorption of the basic dye on activated carbon.

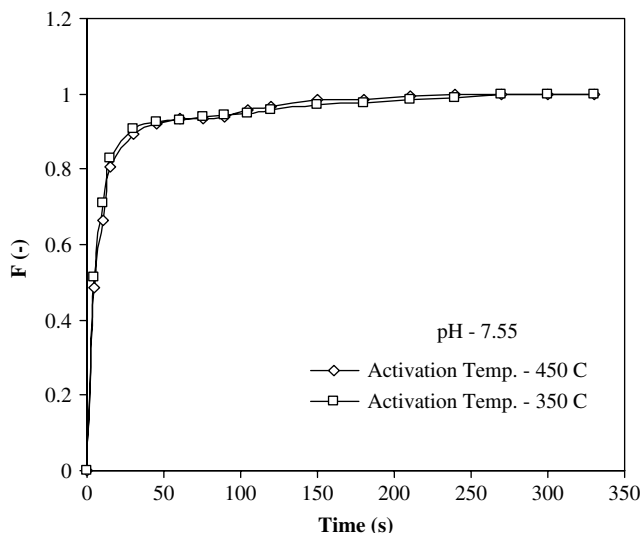
the equilibrium data shows a best fit in the Langmuir isotherm when compared with the Freundlich isotherm or Linear isotherm. This is in accordance with the shape of the sorption isotherms, which correspond to type L2 (Langmuir type) in the<sup>[18]</sup> classification system for adsorption of a solute from its solution. The  $q_0$ (mg/g) value calculated using the slopes and intercept of Langmuir isotherm plot which is listed in the Table 1 shows the degree of adsorption capacity corresponding to the monolayer coverage of binding of sites available in the carbon surface. Maximum value of  $q_0$  was observed for high-temperature activation and for a lower range of initial concentration. The  $K_L$  (l/g) value shows the requirement of activated carbon for a known volume of dye solution. From the table, it was observed that the higher value of  $K_L$  was observed for a high activation temperature and for a low concentration of solution. From this, it is further confirmed that maximum adsorption can be achieved using activated carbon produced at 450 °C, at an initial dye concentration of 40–60 ppm.

## Kinetic study

The effects of contact time of MG for different activation temperatures and for two different initial dye concentrations were studied. Fig. 14 shows the effect

**Table 1. The characteristic parameters of the sorption process of basic dye Malachite Green onto activated carbon.**

T (°C)	Linear isotherm		Freundlich isotherm			Langmuir isotherm		
	K (l/g)	R <sup>2</sup>	K <sub>F</sub> (mg/g)(l/g) <sup>1/n</sup>	N	R <sup>2</sup>	q <sub>0</sub> (mg/g)	K <sub>L</sub> (l/g)	R <sup>2</sup>
350 °C	3.3509	0.9228	1.9561	1.2386	0.9488	172.41	0.0029	0.9973
450 °C	4.3285	0.9781	2.1304	1.2515	0.9166	769.23	0.0056	0.9914



**Figure 14.** The fractional attainment of equilibrium ( $F$ ) vs time for the sorption of the basic dye on activated carbon.

of contact time on the adsorption capacity. From the figure, it was observed that the equilibrium was reached at 330 min in the case of 350 °C activation, and 270 min in the case of 450 °C activation, which shows that the pore formation was good at 450 °C activation temperature when compared to low temperature activation. The SEM image (Figs. 4 and 5) also proves that the 450 °C activated carbon has more number of micropores and micro grooves on its surface compared to 350 °C activated carbon. The presence of these micropores and microgrooves enhances the penetration of dye molecules into the activated carbon and increases the absorbance capacity.

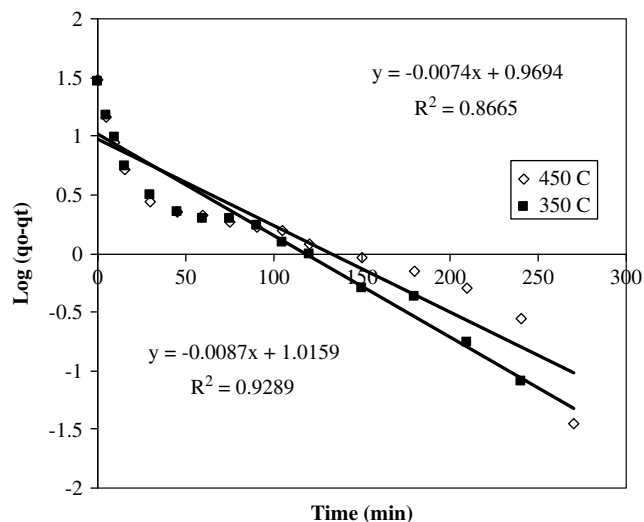
The kinetics of basic dye sorption onto activated charcoal was investigated using two different models: the pseudo-first-order and pseudo-second-order kinetics. The pseudo-first-order Lagergren model, traditionally used for describing sorption kinetics, is generally expressed by Eqn (6)<sup>[19,20]</sup> where  $K_1$  (mg/g/min) is the Lagergren rate constant of the first-order sorption evaluated from the slope of the plot  $\log(q_0 - q_t)$  versus  $t$  (Fig. 15)

$$\text{Log}(q_0 - q_t) = \text{Log}(q_0) - K_1 \cdot C \quad (6)$$

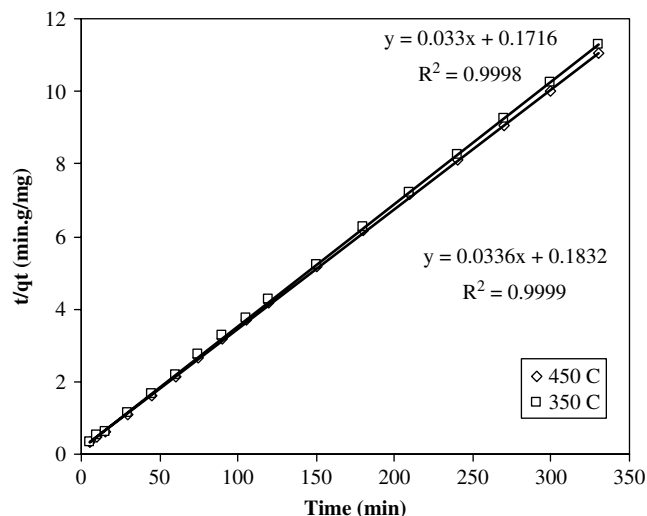
According to the pseudo-second-order model<sup>[21]</sup> the dye sorption kinetic is described by Eqn. (7), where  $K_2$  is the rate constant of second-order sorption (g/mg/min) and  $K_2 \cdot q_0^2 = h$  is the initial sorption rate (mg/g/min).

$$(t/q_t) = (1/K_2 \cdot q_0^2) + (t/q_0) \quad (7)$$

By plotting  $t/q_t$  versus  $t$  (Fig. 16), a straight line could be obtained, and  $q_0$ ,  $K_2$  and  $h$  can be calculated. The experimental kinetic data were adjusted according



**Figure 15.** The applicability of the first-order kinetic models to basic dye sorption on activated carbon.



**Figure 16.** The applicability of the second-order kinetic models to basic dye sorption on activated carbon.

to the indicated models, and the coefficients of correlation as well as the kinetic parameters of dye sorption on activated charcoal are given in Table 2. From the table, it was observed that the pseudo-second-order model provides the best fit compared to the first-order sorption model. This clearly indicates that the adsorption of MG on activated carbon of the palm male flower follows a pseudo-second-order kinetic model and the intra-particle diffusion is the rate-controlling step.

## CONCLUSION

The present investigation shows that the *Borassus flabellofer* male flower (PMF) can be used as one

**Table 2. The kinetics parameters of the sorption process of basic dye Malachite Green onto activated carbon.**

T (°C)	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model		
	K <sub>1</sub> (mg/g/min)	R <sup>2</sup>	K <sub>2</sub> (g/mg/min)	h (mg/g/min)	R <sup>2</sup>
350 °C	0.0087	0.9289	6.16 × 10 <sup>-3</sup>	5.4585	0.9999
450 °C	0.0074	0.8665	6.38 × 10 <sup>-3</sup>	5.8275	0.9998

of the best sources for the production of activated carbon under normal activation, which has higher adsorption capacity towards MG. The sorption of MG from aqueous solution using PMF-activated carbon is a function of initial pH, activation temperature, initial dye concentration, amount of carbon loading and contact time. After analysing these variables, it was concluded that maximum dye removal was achieved at an activation temperature of 450 °C, initial pH of 7.55, initial dye concentration of 40–60 mg/l, and carbon loading of 0.025 mg. The equilibrium sorption data at different temperatures fitted well to the two-parameter monolayer Langmuir model. The kinetic sorption data fitted well to the second-order kinetic model, indicating an intra-particle diffusion mechanism.

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