# Removal of Malachite Green from aqueous solution using degreased coffee bean

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## ARTICLE INFO

## ABSTRACT

This study reports on the feasibility of employing degreased coffee beans (DCB) as adsorbent for Malachite Green (MG) removal in dyeing wastewater. The iodine value (IV), specific surface area (SSA) and porosity of the raw coffee beans (RCB) used in the study increased after the degreasing process, resulting in significant increase in the adsorption of MG onto DCB. Employing a batch experimental set-up, optimum conditions for complete color removal and adsorption of MG by DCB was studied considering parameters such as effect of degreasing process, adsorbent dosage, initial dye concentration, reaction temperature and pH. Adsorbed amount of MG by DCB increased with increasing DCB dosage and initial MG concentration. The rate of the adsorption reaction followed the pseudo second-order kinetics with the sorption isotherm well fitted to the Freundlich and the Langmuir isotherm models. Thermodynamic studies revealed that the adsorption processes is spontaneous and endothermic in nature. DCB has potentials for application as adsorbent for the removal of MG from dyeing process wastewater.

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## 1. Introduction

Dyeing and finishing processes from industries do generate large amounts of colored wastewater which are discharged into natural streams with undesirable consequences to the environment and human health. Apart from the unpleasant aesthetic aspects of dye wastewater, its presence in natural streams can cause serious harm to aquatic life by increasing toxicity, chemical oxygen demand, and as well hindering photosynthetic phenomena through reduction of light penetration [1]. Dyes, such as Malachite Green (MG), though found useful in many industrial applications (dyeing of silk, leather, plastics, paper and others), can cause injuries to humans and animals by direct contact of inhalation and ingestion [2]. Effects such as carcinogenesis, mutagenesis, teratogenesis, respiratory toxicity and reduced fertility in humans have been reported [3]. MG has a complicated chemical structure (Fig. 1); it is resilient to fading on exposure to light and water and is, therefore, difficult to be removed from wastewaters by commonly used techniques such as biological treatment and chemical precipitation. However, since it dissociates in aqueous solutions, it is prone to be strongly adsorbed into solids such as coffee beans.

Globally, coffee has become an established food beverage with its discharge after processing forming large coffee grounds. Part of coffee grounds are reused as compost and animal feed but greater part are burnt as waste which results in production of carbon dioxide, the green house gas [4].

Adsorption processes are being employed widely for large-scale biochemical, chemical, environmental recovery and purification applications [5]. Adsorption application follows a simple design, ease of operation and guarantees relatively high efficiency. Adsorption processes using activated carbons have been widely proposed and used for the removal of both organic and inorganic pollutants from aqueous effluents. However, commercially available activated carbons are expensive and, in recent years, a great deal of effort has been put into the proposal and usage of low-cost adsorbents prepared from naturally occurring materials and wastes for the removal of dyes from wastewaters. Agricultural wastes are the chief raw materials being studied for this purpose, for they are renewable, usually available in large amounts and potentially less expensive [5–8].

To date, adsorbent such as neem sawdust, rattan sawdust, bentonite clay, bottom ash, orange peel, algae and rice straw have been evaluated for use in the removal of Malachite Green from aqueous solution [6,9–11]. This study reports for the first time, on the feasibility of applying degreased coffee beans (DCB) as low-cost alternative adsorbent for Malachite Green color removal from aqueous solution by focusing on the use of discarded (bad) coffee beans. The effects of adsorbent dosage, initial MG concentration, reaction temperature and pH on MG adsorption onto DCB were studied. Adsorption kinetics, isotherms and thermodynamic parameters were also evaluated and reported.

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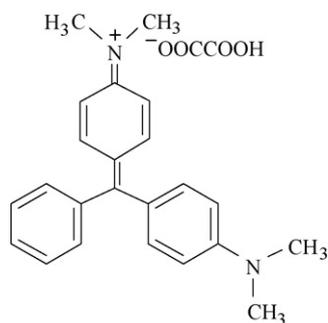
**Fig. 1.** Chemical structure of Malachite Green.

## 2. Materials and methods

### 2.1. Adsorbent preparation and characterization

There are two species of coffee: Arabica (75% of world coffee production) and Robusta. Arabica coffee bean from Kirkland Signature was used in the study. The raw coffee beans (RCB) were cut into two in order to extract the coffee entirely from its husk. They were washed in warm water (50 °C) and dried in an oven at 105 °C for 24 h. The degreasing of RCB was carried out by contacting 2 g of RCB with 20 mL of NaOH solution at different concentrations (0.01–5 M) for 1–720 min at 25 °C in a mechanical shaking incubator operated at 200 rpm. Substrate (DCB) was filtered, dried and sieved to obtain a grain size of 4–8 mm.

The influence of the degreasing process on the iodine value (IV) and the specific surface area (SSA) of RCB were studied in order to evaluate its adsorption capacity. The IV was estimated using the methods of [12] and the SSA was measured using the EGME method [13]. Also, SEM (Scanning Electron Microscopy) was employed for the observation of the surface microporous structure. Infrared spectroscopy analysis was carried out using Jasco FT/IR-300E spectrometer with Fourier Transformed (FT-IR) recorded in the region 2000–600 cm$^{-1}$ at 4 cm$^{-1}$ resolutions.

### 2.2. Batch adsorption experiment

To estimate the applicability of DCB as adsorbent for dye wastewater treatment, adsorption test was performed using MG as the adsorbate. Stock solution of MG was prepared by dissolving an appropriate amount of N,N,N,N-tetramethyl-4,4′-diaminotriphenylcarbenium oxalate in three times distilled water (>18 MΩ). A range of dilutions (25–100 mg/L) from the stock solution was done to obtain the initial MG concentrations used in the study. Equilibrium experiments were carried out by contacting 0.1 g of RCB and DCB with 50 mL of MG solution at different initial concentrations. For optimization of experimental conditions like temperature, adsorbate concentration and contact time, batch experiment were performed with the sorbent–sorbate suspension in a 100 mL conical flask, at 25 °C and 200 rpm in a mechanical shaking incubator equipped with a temperature controller. To examine the effect of temperature on the adsorption process, the temperature of the adsorbate solution was controlled between 25 °C and 45 °C. Observations on pH effects were measured at pH values ranging from pH 2–10. The pH of the solution was controlled with 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Samples were prepared for each reaction time instead of sampling from a single flask, so that the concentration of the remaining adsorbate remained constant. After the reaction, the adsorbent was removed by centrifugation followed by analysis of the filtrate for residual MG concentration using Spectronic 20D (Miton Roy Co.) at a wavelength of 617 nm corresponding to the maximum absorbance ($\lambda_{max}$) for MG.

The feasibility of DCB reuse was assessed using desorption and regeneration processes. Desorption experiments were performed using 0.1 M HCl in a batch experimental study. The MG loaded DCB was washed with deionised water respectively to remove any unadsorbed MG. The spent DCB was then re-suspended in 50 mL of 0.1 M HCl following the same equilibrium condition for the adsorption process. The solution mixture was filtered and the adsorbent washed several times with distilled water in order to remove excess acid. It was then treated with 50 mL of MG solution at 50 mg/L. The above procedure was repeated for three cycles.

### 2.3. Calculation

The amount of MG adsorbed by the adsorbent ($q_t$,) at each time interval t, was calculated using the mass balance equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

and the amount of MG removed (%) was calculated using Eq. (2):

$$\text{Removal}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

where $q_t$ is the amount of MG adsorbed per unit weight of adsorbent at any time t (mg/g); $C_0$ and $C_t$ are the initial and liquid-phase concentrations of the MG solution at any time t (mg/L), respectively; V is the volume of the MG solution (ca. 0.05 L); and m is the amount of the sorbent used.

The amount of dye desorbed was calculated from the concentration of desorbed dye in the liquid phase. The percentage of MG desorbed from DCB is calculated as: Desorption (%) = (Mass of dye desorbed/Mass of dye adsorbed) × 100%.

## 3. Results and discussion

### 3.1. Characterization of adsorbent

The change in iodine value was investigated as a function of treatment time for different NaOH concentration (Fig. 2). With increase in treatment time of RCB using NaOH, iodine values increases. In Table 1, IV increased gradually with NaOH concentration. The iodine value could be another means of assessing information on the surface area and adsorption capacity of a material. Determination of iodine value is usually a complimentary test to the N$_2$/77 K adsorption isotherms, and assumed to measure the
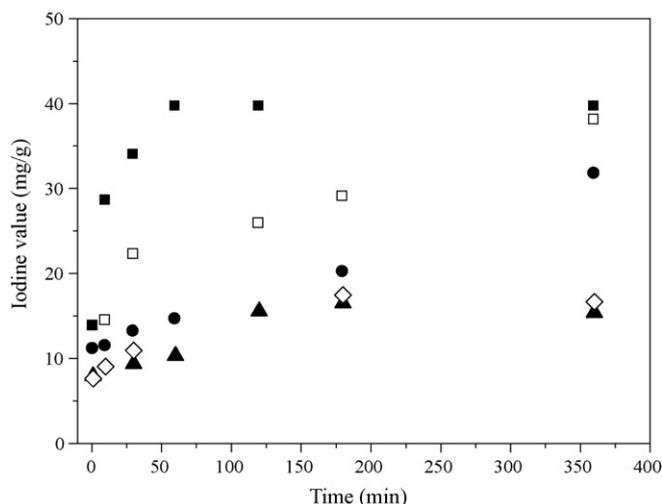


**Fig. 2.** Changes in iodine value of RCB according to NaOH concentrations (▲: 0.01 M NaOH, ◇: 0.1 M NaOH, ●: 1 M NaOH, □: 2 M NaOH, ■: 5 M NaOH).

**Table 1**
Iodine value and specific surface area of RCB and DCB according to NaOH treatment concentration.

| | Raw coffee beans | Degreased coffee beans | | | | |
|---|---|---|---|---|---|---|
| | | 0.01 M | 0.1 M | 1 M | 2 M | 5 M |
| Iodine value (mg/g) | 9.84 | 15.39 | 16.66 | 31.37 | 38.07 | 39.66 |
| Specific surface area (m$^2$/g) | 120 | 142.1 | 155.7 | 161.3 | 171.9 | 173.2 |

surface area in micropores within pore sizes of a material. Increase in IV values of an adsorbent portrays that the adsorption capacity of such adsorbent is good [14]. From Table 1, it can be observed that RCB seems to have possessed appreciable narrow micro-porosity unavailable to iodine while the adsorbed amount of iodine is higher for DCB. This result is presumably due to change in the microporous structure of DCB. With the application of NaOH on RCB, the oily content of RCB reduces; NaOH has been reported as an effective alkaline degreasing solution for oil removal from material surfaces [15]. Oil acts as film on surfaces of materials and as well reduces porosity (block pores) therefore, treatment of RCB with NaOH enhanced the surface area of RCB, making it more porous, and with increasing concentration of NaOH, porosity increases hence, iodine adsorption increases. Invariably too, adsorption capacity will increase.

With the IV values for 2 M and 5 M of NaOH being very close, 2 M of NaOH is chosen in the study as appropriate concentration of NaOH for the degreasing of RCB, considering the cost of the degreasing process. Specific surface area of RCB was 120 m$^2$/g, and as NaOH concentration increases, the SSA of RCB also increases.

The microstructures of RCB and DCB at different NaOH concentrations were observed by SEM (Fig. 3). The DCB structure becomes more porous as concentration of NaOH increases, RCB as well possess some micropores (Fig. 3a). Little differences can be identified in both RCB and DCB spectra (Fig. 4), particularly in the regions 900–1300 cm$^{-1}$. However, there is a need to obtain a definitive dif-

ferentiation between the two species. The FT-IR spectrum band at 1100–1300 cm$^{-1}$ for RCB (Fig. 4a) may be assigned to coffee oil, this peak was removed by the degreasing treatment. According to literature [16,17], the bands in the 1200–900 cm$^{-1}$ range are assigned to $m$(S=O), showing the existence of sulphur and the peak for carboxyl linkage derived from xanthine derivatives such as caffeine, do appear at approximately 1550–1750 cm$^{-1}$, and as shown in Fig. 4, this peak appeared in both RCB and DCB with the bands at this region remaining unchanged, thus, caffeine was not removed by the degreasing treatment.

### 3.2. Adsorption studies

#### 3.2.1. Effect of degreasing treatment and DCB dosage

The removal of MG by RCB and DCB were investigated (Fig. 5). MG adsorption onto DCB occurred within 1 h and reached almost equilibrium in about 4 h for the investigated range of MG concentrations. MG removal by RCB increased slowly at the incipient stage of adsorption, and reached equilibrium in about 8 h. As shown in Fig. 5, MG removal using DCB was greater compared to MG removal by RCB.

With increase in DCB dosage, the adsorption of MG increased (Fig. 6). Keeping adsorbate concentration fixed and increasing the amount of sorbent, makes a large number of sites available for a fixed concentration of MG, hence the increase in extent of adsorption.
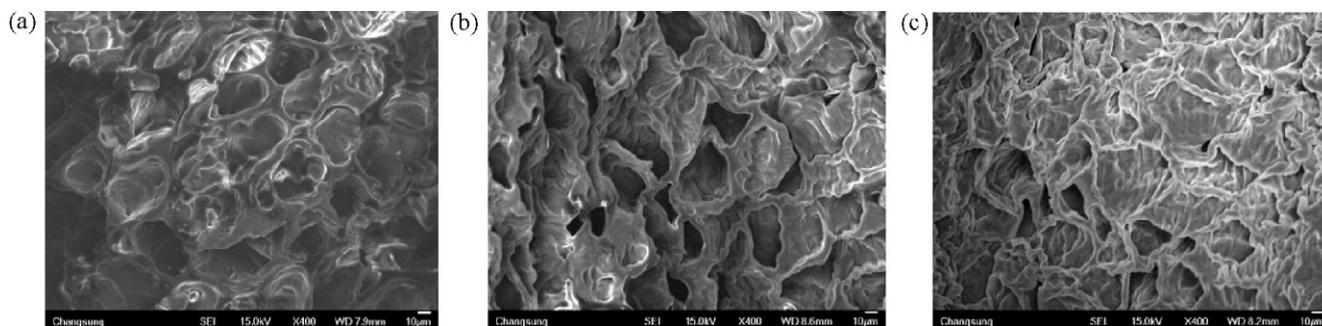


**Fig. 3.** SEM morphologies of (a) RCB, (b) DCB obtained from RCB treatment with 0.1 M NaOH for 6 h, and (c) DCB obtained from RCB treatment with 2 M NaOH for 6 h.
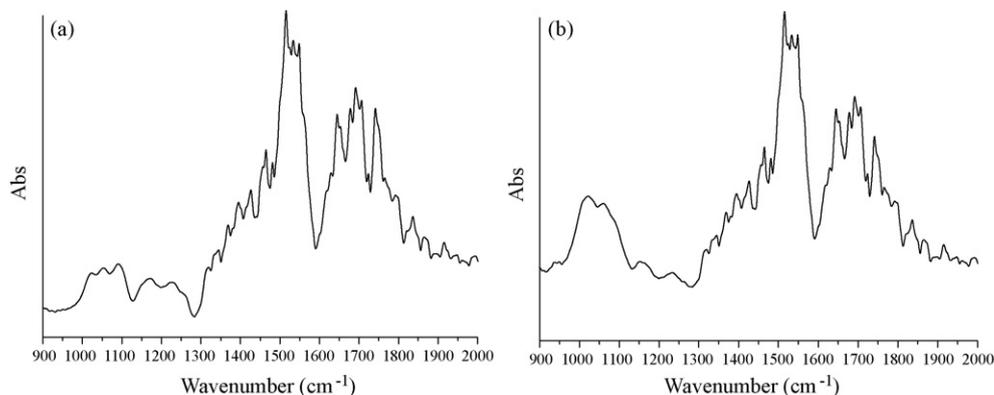


**Fig. 4.** FT-IR spectra for (a) RCB, (b) DCB.
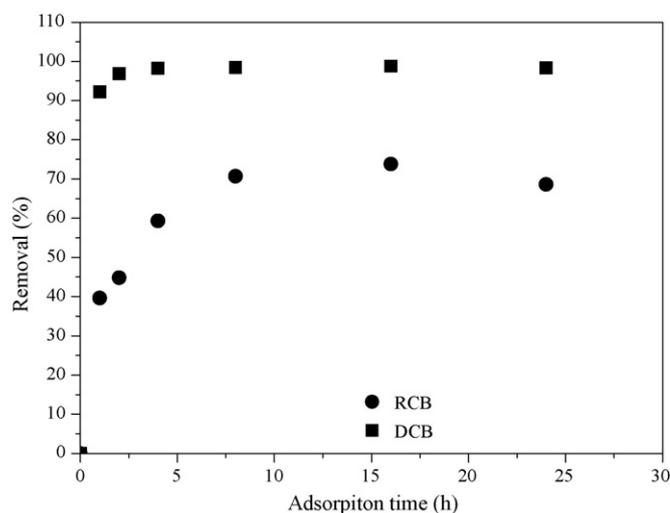
**Fig. 5.** Removal of MG according to adsorption time (initial concentration of MG: 25 mg/L, adsorbent dosage: 2 g/L, pH: 4 ± 0.1, temperature: 25 ± 0.1 °C).



**Fig. 6.** Adsorbed amount (%) of MG by DCB at different adsorbent dosage (initial concentration of MG: 100 mg/L, pH: 4 ± 0.1, temperature: 25 ± 0.1 °C).

### 3.2.2. Effect of initial MG concentration

The contact time necessary to reach equilibrium depends on the initial dye concentration [18]. The effect of contact time on the adsorption of MG onto DCB at different initial MG concentrations is presented in Fig. 7. Absolute amount of adsorbed MG at equilibrium condition decreased as MG concentration decreases. It could be said that the higher the adsorbate concentration, the more diffusion would occur from the adsorbent surface into the micropores. Maximum adsorbed amount for MG onto DCB was achieved within 30 min for 0.3 g of DCB employed, increasing concentration gradient, acts as increasing driving force, and in turn leads to an increasing equilibrium sorption until sorbent saturation is achieved [19]. The adsorption capacity at equilibrium increased, while the



**Fig. 7.** Equilibrium sorbed amount of MG onto DCB according to adsorption time at various initial MG concentrations (adsorbent dosage: 6 g/L, pH: 4 ± 0.1, temperature: 25 ± 0.1 °C).

percentage of adsorption decreased from 84.6% to 78.6% as the initial MG concentration increased from 25 mg/L to 100 mg/L. The fast uptake of MG molecules is traceable to solute transfer, as there are only sorbate and sorbent interactions with negligible interference from solute–solute interactions. The initial rate of adsorption was therefore greater for high initial MG concentrations, the resistance to the MG uptake diminished as the mass transfer driving force increased [18].

### 3.2.3. Adsorption kinetics

The kinetics of the adsorption process was analyzed using the pseudo first-order and pseudo second-order equations to model the kinetics of MG adsorption onto DCB.

The pseudo first-order equation of Lagergren [20] is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where $k_1$ is the rate constant of the pseudo first-order adsorption (min$^{-1}$), $q_t$ (mg/g) is the amount of MG adsorbed at various times $t$, and $q_e$ (mg/g) is the amount of MG adsorbed onto DCB at equilibrium. After integrating with the initial conditions, the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The slope and the intercepts of the plots of $\log(q_e - q_t)$ versus $t$ were obtained to determine $k_1$ and $q_e$ (plots not shown). The values obtained for $k_1$ and $q_e$ are presented in Table 2. Adsorption of MG onto DCB may also have followed the pseudo first-order mechanism as the $q_{e,calc}$ agreed well with the experimental data ($q_{e,exp}$) at some studied concentration. However, the $R^2$ values (Table 2) for the Lagergren model at different concentrations were relatively low, particularly at low concentrations. The calculated $q_e$ values obtained from the model at these concentrations, failed to match

**Table 2**
Kinetic parameters for MG adsorption onto DCB.

| Initial concentration (mg/L) | $q_{e,exp}$ (mg/g) | First-order kinetics | | | Second-order kinetics | | |
|---|---|---|---|---|---|---|---|
| | | $k_1$ | $q_{e,cal}$ (mg/g) | $R^2$ | $k_2$ | $q_{e,cal}$ (mg/g) | $R^2$ |
| 25 | 4.02 | 0.189 | 4.71 | 0.9157 | 0.323 | 4.07 | 0.999 |
| 50 | 7.99 | 0.223 | 28.2 | 0.8873 | 0.0565 | 8.33 | 0.999 |
| 75 | 11.99 | 0.142 | 13.5 | 0.9926 | 0.0109 | 13.66 | 0.993 |
| 100 | 16.07 | 0.103 | 17.1 | 0.9914 | 0.00375 | 20.26 | 0.992 |

the experimental $q_e$ values and in comparing the $R^2$ values of the Lagergren model with that of the pseudo second-order model in Table 2, the adsorption of MG onto DCB can be said not to have followed the first-order reaction model as the $R^2$ values from the pseudo second-order model were closer to unity than of the Lagergren.

The pseudo second-order model [21] can be represented in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where $k_2$ is the rate constant of pseudo second-order model (g/mg/min). After integrating with the initial conditions, Eq. (5) takes the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

$k_2$ and the equilibrium adsorption amount $q_e$ were determined from the slope and intercept of the plot of $t/q_t$ versus $t$. The correlation coefficient ($R^2$) for the pseudo second-order kinetic at different initial MG concentrations, were above 0.992 and the calculated $q_e$ values were close to the experimental values (Table 2). The adsorption kinetics of MG onto DCB may have obeyed the pseudo second-order kinetic model. Yeddou and Bensmaili presented similar results for the sorption systems of dye from aqueous solution by clay-wood sawdust mixture [22]. The equilibrium sorption capacity $q_e$ in this study, increased from 4.07 mg/g to 20.26 mg/g when the initial concentration of DCB increased from 25 mg/L to 100 mg/L. The values of the rate constant were found to decrease from $3.23 \times 10^{-1}$ g/mg min to $3.75 \times 10^{-4}$ g/mg min for an increase in the initial concentration from 25 mg/L to 100 mg/L. Previous literature reported that the kinetics of the sorption of MG onto orange peel, bentonite and *Arundo donax* root followed the pseudo second-order reaction rate [11,19,22].

### 3.2.4. Adsorption isotherms

Adsorption equilibrium isotherm is expressed by relating the amount of adsorbate taken up per gram of adsorbent, $q_e$ (mg/g), to the equilibrium solution concentration, $C_e$ (mg/L), at a fixed temperature. Generally, adsorption isotherms provide vital information in optimizing the use of adsorbents. Freundlich and Langmuir models are commonly used to describe adsorption isotherms, and their constants provide significant parameters for predicting adsorption capacities [23,24].

The widely used empirical Freundlich equation [25] based on heterogeneous surface sorption is expressed by:

$$q_e = K_F C_e^{1/n} \tag{7}$$

This equation can be linearized as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{8}$$

where $q_e$ is the solid phase equilibrium amount of MG adsorbed per unit weight of the adsorbent (mg/g); $C_e$ is the equilibrium concentration of MG in solution (mg/L). The values of $n$ and $K_F$ were calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$. The Freundlich constant $K_F$ indicates the adsorption capacity of the adsorbent and $n$ is a measure of the deviation of the model from linearity of the adsorption.

The Langmuir equation [26] is probably the best known and most widely applied adsorption isotherm. It is represented as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

**Table 3**
Freundlich and Langmuir isotherm parameters for MG adsorption onto DCB.

| Temp (°C) | $q_e$ | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|---|
| | | $K_F$ | $n$ | $R^2$ | $q_m$ | $K_L$ | $R^2$ |
| 25 | 23.00 | 2.03 | 0.511 | 0.995 | 55.3 | 0.0935 | 0.994 |
| 35 | 5.73 | 0.079 | 0.287 | 0.965 | 36.2 | 0.0828 | 0.984 |
| 45 | 28.40 | 0.007 | 0.210 | 0.982 | 24.8 | 0.1004 | 0.987 |

A linear form of this expression is:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m} \tag{10}$$

where, $q_m$ is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g); $K_L$ is a direct measure of the intensity of adsorption (L/mg). From the plot of $1/q_e$ versus $1/C_e$, $K_L$ and $q_m$ can be estimated from the slope and intercept of the plot.

Correlation coefficients and parameter values for both isotherms were presented in Table 3. Based on the correlation coefficients, the applicability of the isotherms was compared (Table 3). The experimental results indicated that the sorption of MG onto DCB followed both Freundlich and Langmuir models. Similar observation was reported for adsorption of Congo Red on activated carbon [27], and also for the adsorption of Methyl Orange, Congo Red, Methylene Blue, and Rhodamine B on waste banana peel [28]. Ideally, a wide range of $C_e$ values are necessary to discuss the Freundlich model of adsorption. From Table 3, the monolayer adsorption capacity decreases with increase in temperature. $q_e$ from the Freundlich isotherm does not show a trend, therefore, the adsorption process may have followed the Langmuir isotherm.

If the value of the Freundlich parameter $n$ is below unity, it implies that the adsorption process is chemical, and if $n$ is above unity, it is a physical adsorption process [29]. As shown in Table 3, $n$ value at equilibrium was 0.51, indicating a chemosorption adsorption of MG onto DCB.

To determine if adsorption process is favorable or unfavorable for Langmuir type adsorption process, Langmuir isotherm is then classified using a dimensionless constant separation factor ($R_L$), which can be defined as [30]:

$$R_L = \frac{1}{1 + bC_o} \tag{11}$$

$C_o$ is the initial concentration of MG (mg/L); $b$ is the Langmuir isotherm constant. If the value of $R_L < 1$, it indicates a favorable adsorption and if $R_L > 1$ then, an unfavorable adsorption. The $R_L$ values for the adsorption of MG onto DCB was in the range $0 < R_L < 1$ (Fig. 8), indicating that Langmuir adsorption is favorable for the adsorption of MG onto DCB.

### 3.2.5. Dubinin–Radushkevich (D–R) isotherm

The D–R model describes adsorption on both homogenous and heterogeneous surfaces [31]. The model is an analogue of the Langmuir isotherm but more general than the Langmuir as it rejects the homogeneous surface or constant adsorption potential as expressed in Tempkin isotherm [29]. It provides estimation of adsorbents characteristic porosity and as well their apparent energies of adsorption. The model has a linear form expressed as:

$$\ln q_e = \ln q_{DR} - \gamma \varepsilon^2 \tag{12}$$

where $q_{DR}$ is the D–R adsorption capacity (mg/g), $\gamma$ is the adsorption energy constant (mol$^2$/kJ$^2$) and $\varepsilon$ is the Polanyi potential [32] which is defined as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{13}$$
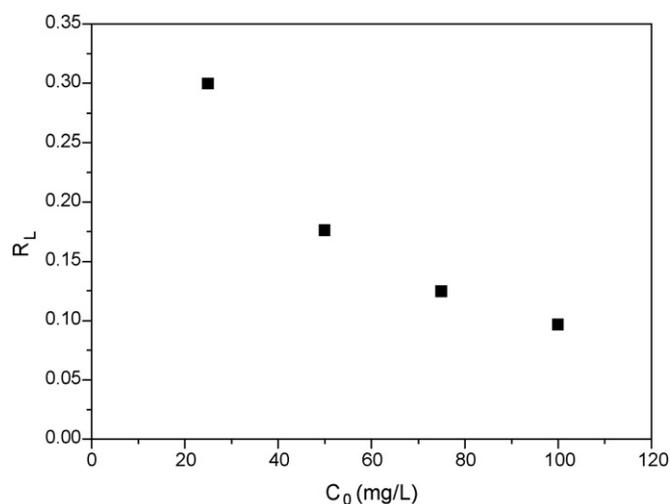
Fig. 8. Freundlich and Langmuir isotherms for adsorption of MG onto DCB.

$R$ and $T$ are the gas constant (8.314 J/mol K) and the absolute temperature, respectively. With the values of $\gamma$, the mean sorption energy ($E$) which is the free energy for the transfer of 1 mol of MG from infinity to the surfaces of DCB can be estimated as follows:

$$E = -\frac{1}{\sqrt{2\gamma}} \qquad (14)$$

For values of $E < 8$ kJ/mol, physical forces may have effect on the adsorption mechanism while $E$ values between 8 kJ/mol and 16 kJ/mol depicts the adsorption is being controlled by ion exchange and $E > 16$ kJ/mol signifies an adsorption governed by particle diffusion mechanism [29]. The adsorption energy, $E$, was found to be 223 kJ/mol for DCB, confirming that the adsorption of MG onto DCB is controlled by a chemical process.

### 3.2.6. Activation energy, thermodynamic parameters and effect of temperature

A study of temperature dependence during adsorption process gives valuable information about the enthalpy and entropy changes accompanying adsorption processes [33]. The effect of temperature on the adsorption of MG at 100 mg/L, onto DCB as a function of time is presented in Fig. 9. The equilibrium adsorption capacity was affected by temperature. This indicates that temperature has
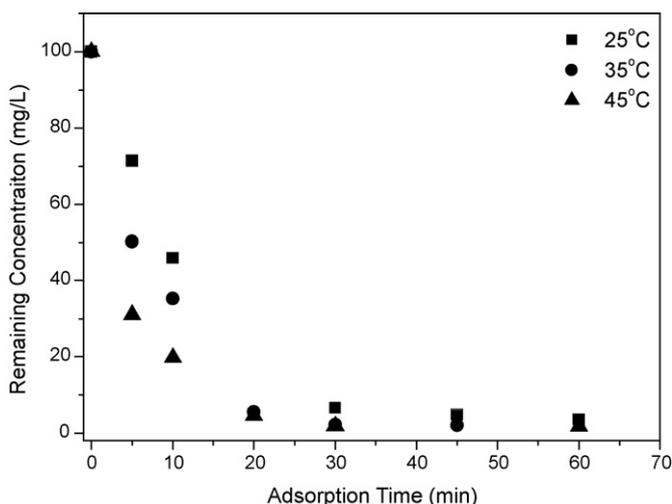


Fig. 9. Separation factor plot for MG adsorption onto DCB.
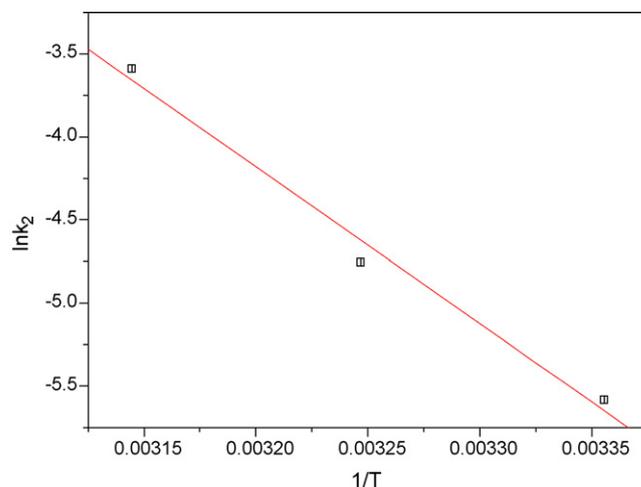


Fig. 10. Changes in remaining concentration of MG according to adsorption time at different temperatures (MG concentration: 100 mg/L, adsorbent dosage: 6 g/L, pH: 4 ± 0.1).

an effect on adsorption of MG by DCB and that the process is also endothermic in nature.

Using the Arrhenius equation [10]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (15)$$

where $E_a$ is the activation energy (J/mol), $k_2$ is the pseudo second-order rate constant for adsorption (g/mol s), $A$ is the temperature-independent Arrhenius factor (g/mol s), $R$ is the gas constant (8.314 J/K mol), and $T$, the solution temperature (K); it is possible to gain some insight into the type of adsorption taking place between the MG molecules and the DCB surface. The slope of the plot of $\ln k_2$ versus $T^{-1}$ (Fig. 10) can be used to evaluate $E_a$. Generally, low activation energies (5–40 kJ/mol) are characteristic of physical adsorption, while high ones (40–800 kJ/mol) suggest chemisorptions [18]. In this study, $E_a = 78.5$ kJ/mol for the adsorption of MG onto DCB, indicating that the rate-limiting step in the adsorption process, might be a chemically controlled type. Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and, like most chemical reactions, it frequently involves an energy of activation.

Thermodynamic parameters are important in adsorption studies for better understanding of the effect of temperature on adsorption. In physicochemical reactions, of which adsorption reactions are inclusive, the relationship between equilibrium constant and temperature under an assumption that $\Delta H^\circ$ is constant within the range of temperatures studied can be expressed by the van't Hoff equation [33]:

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H^\circ}{R} \qquad (16)$$

where $K$ is the equilibrium constant, $T$, is the absolute temperature (K), $\Delta H^\circ$, is the enthalpy (kJ/mol) and $R$, is the universal gas constant (8.314 J/mol K). The equilibrium constant, $K$, can be defined as:

$$K = \frac{C_{ads}}{C_e} = \frac{C_0 - C_e}{C_e} = \frac{C_0}{C_e} - 1 \qquad (17)$$

where, $C_0$ (mg/L) and $C_e$ (mg/L) represent the concentration of adsorbate which is initially adjusted and remaining in solution at equilibrium, respectively. The value of $\Delta H^\circ$ was calculated from the slope of the linear regression of $\ln K$ versus $1/T$ (Fig. 10).

Thermodynamic parameters for adsorption, such as $\Delta G^\circ$ and $\Delta S^\circ$ can also be obtained from the calculated $\Delta H^\circ$ using the fol-

**Table 4**
Thermodynamic parameters for MG adsorption onto DCB.

| Temperature (°C) | $k_2$ | $K$ | $\Delta G°$ (kJ/mol) | $\Delta S°$ (J/K mol) | $\Delta H°$ (kJ/mol) |
|---|---|---|---|---|---|
| 25 | 0.00375 | 27.3 | −8.19 | 27.6 | |
| 35 | 0.00861 | 50.1 | −10.0 | 32.6 | 27.2 |
| 45 | 0.0276 | 54.1 | −10.6 | 33.3 | |

lowing relations:

$$\Delta G° = -RT \ \ln K \tag{18}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{19}$$

The estimated thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ and equilibrium constants at each temperature are summarized in Table 4.

The enthalpy change ($\Delta H°$) for the adsorption of MG onto DCB signifies an endothermic adsorption. Similar results have been reported for MG adsorption onto bentonite, activated carbon prepared from de-oiled soya and activated carbon prepared from Tuncbilek lignite [34,35]. The $\Delta G°$ value is negative at all studied temperatures, inferring that, the adsorption of MG onto DCB will follow a spontaneous trend. The $\Delta G°$ value decreased when the temperature increased from 25 °C to 45 °C, suggesting increase in adsorption of MG with increasing temperature [8]. The positive value of $\Delta S°$ reflects the affinity of DCB towards MG [22,35] and also suggests increased randomness at the solid–solution interface.

### 3.2.7. Effect of pH on color removal

One of the most important factors affecting the capacity of an adsorbent in wastewater treatment is pH. The effect of pH on MG color removal by DCB is shown in Fig. 11. The percentage color removal of MB increased from 66% to 95% with increase in pH from 2 to 6. The removal then slowly increases at pH beyond 6 till it attains a constant value. Maximum color removal was observed at pH 10–12. There was no significant change in color removal after pH 6, it was has been reported that increase in dye adsorption depends on the properties of the adsorbent surface and the dye structure [8,9]. This behavior clearly indicates the protonation of MG in acidic medium and with the rise in pH the dye becomes more and more de-protonated. In lower pH range, the low color removal also display the possibility of positive charge development at the DCB surface, which inhibits color removal from the dye [10]. However, beyond pH 6 in the basic medium there seems to be an insignificant change in polarity as color removal increases monotonically with pH. Maximum MG color removal (98%) occurred over the pH range of 10–12. Low pH (<4) was unfavorable for MG color removal by DCB. As initial pH (natural pH 4) of MG solution decreases, the number of negatively charged adsorbent sites decreases and positively charged sites increases, which does not favor the adsorption
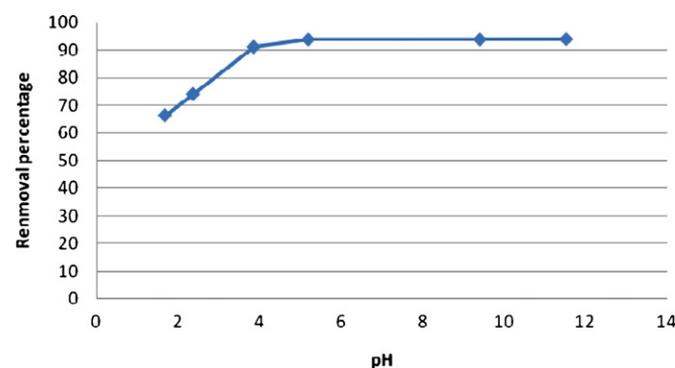
of positively charged MG cations [36] due to electrostatic repulsion. A similar behavior for MG onto has been reported [37] and as well for the removal of basic dye from aqueous solutions using spent tea leaves [38].

### 3.2.8. Desorption studies

For economical adsorption process, it is necessary to regenerate spent adsorbent, therefore, the desorption test on spent DCB using 0.1 M HCl solution as observed after three cycles showed that the reversibility of DCB decreased and only a small amount of dye desorbed from DCB. The sorption capacity of DCB decreased from 96.4% to 52.5%. The recovery of MG using 0.1 M HCl decreased from 28.3% in the first cycle to 9.4% in the third cycle. However, the adsorbed MG desorbed but desorption was not too significant. Only 0.1 M HCl was used as eluting agent, and as such, conclusion cannot be made in the present study as desorption behavior may differ with varying concentration of HCl and as well with different eluting agents.

The reversibility of adsorption depends on whether there is a strong binding bond such as ionic or covalent bonding or weak binding forces such as Van der Waals' forces or a dipole–dipole interaction formed between the adsorbent surface and the dye molecules. When only weak binding forces (physisorption) are dominant and control the adsorption of reactive dyes onto adsorbent surface, high reversibility of adsorption may occur but when electrostatic interaction between the dye molecules and the surface adsorbent is strong, i.e. chemical reactions occurs between the functional groups on the dye and adsorbent surfaces; then, low reversibility of adsorption occurs. Therefore, different surface characteristics would help to explain the reversibility of adsorption [39].

### 3.2.9. Economic appraisal

The degreased coffee beans used in the study is defected coffee beans which have little or no commercial value in international markets because they affect the quality of the beverage when processed with non defective beans. This waste is collected at coffee mill at no cost; however the handling charges for the collection and transportation will be involved. But the total cost of DCB will be extremely low in comparison to activated carbon and some other adsorbents for MG, therefore, from the view of the cost regenerating DCB, the recovery of MG and the regeneration of DCB may not be cost effective. The MG loaded DCB can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fire briquettes. The ash may be used to make fire-bricks, thus, disposing of MG through chemical fixation. This approach of DCB disposal entails energy recovery from the DCB and the safe disposal of the adsorbed MG.

A rough assessment of the capital cost of using DCB for MG was made based on the saturation capacity of the adsorbent alone, without considering other cost factors such as regeneration or spent adsorbent disposal cost. DCB, activated carbon, char and silica were compared, using the saturation capacity values from experimental equilibrium isotherm data. Adsorption system cost was judged as the relative cost for adsorbing 1 kg of MG dye. Numerous researchers [9,16,40,41] have followed this procedure to calculate the adsorption process cost. Table 5 presents the economic cost and adsorption capacity of MG with adsorbents.



**Fig. 11.** Plots of lnK vs. 1/T for the adsorption of MG onto DCB temperatures (MG concentration: 100 mg/L, adsorbent dosage: 6 g/L, pH: 4 ± 0.1).

**Table 5**
Cost and adsorption (saturation) capacity of DCB in comparison with other adsorbents for adsorption of MG.

| Adsorbent | Saturation capacity (mg/g) | Price/kg of adsorbent compared to activated carbon price | Price/adsorbed kg of MG compared to activated carbon price | Reference |
|---|---|---|---|---|
| CAC MercK | 222.22 | 1 | 1 | [41] |
| DCB | 55.3 | 0.027 | 0.041 | This study |
| Carbonaceous material | 75.1 | 0.14 | 0.57 | [42] |
| Sawdust carbon | 74.5 | 0.17 | 0.48 | [43,44] |

## 4. Conclusion

The study shows that DCB, an agro-based material, can be used as an adsorbent for removal of MG from aqueous solutions. The adsorption characteristics of MG in aqueous solution were shown to be influenced by several factors. The adsorption was highly dependent on initial dye concentration, reaction temperature and pH. The result of the present investigations showed that degreased coffee beans have higher adsorption efficiency than raw coffee beans. The adsorbed amount of MG increased as initial MG concentration increase. Kinetic studies indicated that the sorption might have followed the pseudo second-order kinetic model though the correlations coefficients from the pseudo first-order kinetic were as well relatively high for the range of concentrations studied. MG adsorption onto degreased coffee beans followed both Freundlich model and Langmuir model. Thermodynamic studies showed that the adsorption processes were spontaneous and endothermic since $\Delta G°$ value was negative and $\Delta H°$ value was positive. Increase in MG color removal was observed with corresponding increase in pH from pH 2–6 and then monotonically increase from pH 6 to 12. Coffee beans are abundantly available in the food industry. Taking into consideration all the above obtained results, it can be concluded that DCB can be an alternative material to more costly adsorbents used for dye removal in wastewater treatment processes. Therefore, the use of this low-cost material by small scale dyeing unit using batch or stirred-tank flow reactors is recommended for a direct solution.

## Acknowledgement

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