Scavenging malachite green dye from aqueous solution using durian peel based activated carbon

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**Graphical abstract**

**Abstract**

Physicochemical activation consists of heat treatment coupling with CO2 gasification and KOH chemical treatment were applied in preparing durian peel based activated carbon (DPAC) to remove basic dye, malachite green (MG) from aqueous solution. Several parameters namely, effect of initial MG concentration as well as contact time, solution temperature and initial solution pH were carried out in this study. Characterization study revealed that DPAC pose high BET surface area which is 686.31 m²/g and its surface was found to be mesoporous in nature with heterogeneous type of pore structures. Eight isotherms and four kinetic models were utilized and it was revealed that the adsorption system followed Freundlich isotherm and pseudo-first order (PFO) kinetic model. Mechanism study using intraparticle diffusion and Boyd plot confirmed that adsorption of MG onto DPAC was controlled by the film-diffusion mechanism. Thermodynamic study indicated that the adsorption system was exothermic, spontaneous, feasible and governed by physical-type of adsorption.

**Keywords:** Adsorption, Activated Carbon, Malachite Green, Physicochemical Activation

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**INTRODUCTION**

Growing demand of clothes from increasing population around the globe has accelerated the development in textile industries. This development is directly proportional to the dyes production. Dyes are essential in giving a final beautification touch to the products (Adereimi et al., 2018). It is estimated that 100,000 dissimilar kind of dyes are commercially exist with yearly production of 0.7 million tons (Vega-Negron et al., 2018). Textile industries encompass an integrated activity ranging from pre-treatment, polymerization, spinning, texturizing, dyeing, printing and made up textile goods. In dyeing operation, most of the wastewater comes from wash water, followed by spent dye bath. Due to dyes’ solubility in water, they are easily lost in the effluent during the dyeing processing step (Ahmad et al., 2015). This has been a major concern as it can promote eutrophication and reduce the aesthetic value of the water bodies. Furthermore, the existence of dyes in environment may hurt the textile industries due to their failure to comply with ISO 14000 certification of quality standard specifications (Ayanda et al., 2018).

One of the most popular dye utilized in textile industries is malachite green (MG), a dye that belongs to basic dye group and known as cationic dye. It produces colored cation in solution due to the present of positively charged nitrogen or sulfur atom. MG is applied to paper, polyacrylonitrile, modifiednylon, polyesters, silk, wool and tannin-mordanted cotton by forming salt linkages (ionic bonds) with anionic groups in the fiber. Despite of its versatility, numerous concerns had arisen regarding the expanding use of MG due to its toxicity effects such as cytotoxic, genotoxic and mutagenic (Bhatti et al., 2017). Not only in their original form, but the breakdown products also can be toxic and carcinogenic to the aquatic life (Zhou et al., 2019). Hence, it is essential to treat MG wastewater before entering the environment. Dyes removal techniques can be categorized into biological, chemical and physical treatments. Biological treatment can be further subcategorized into two types; (i) aerobic process which require oxygen for bacteria to perform degradation process (Khouni et al., 2020, Zhu et al., 2020) and (ii) anaerobic process which operates in the absence of air (Bai et al., 2020, Berkessa et al., 2020). Although biological treatment has advantages such as low cost and absence of chemical waste production, the dyes are not biologically degradable since microorganisms do not utilize the dyes as a source of food. Chemical treatment includes the use of coagulation and flocculation agent in removing dyes from wastewater. However, this method is ineffective to treat dyes that have high solubility in water. Other examples of chemical treatments are oxidation process (Mota et al., 2020), photochemical (Bahadori et al., 2020) and electrochemical degradation (Pereira et al., 2020). The major drawback in chemical treatment is that its application can cause concentrated sludge to accumulate, thus required a further treatment or disposal method. Physical treatments on the other hand, comprises of adsorption process. Posing several advantages such as simplicity in design, fast, easy to operate, relatively low operating cost and stable towards toxic substance had cause adsorption process to be a popular choice in treating dye wastewater (Machrouhi et al., 2017). Plus, only half or quarter space is required in adsorption process compared to biological
system. Among of the adsorbents, activated carbon is proved to be the most effective one as it has very porous structure resulting large surface area in range 500–2000 m²/g. This large surface area provides plenty of active sites for the adsorption process to take place. Commercially available activated carbon is produced from non-renewable precursor such as lignite and bituminous coal. These precursors are relatively expensive, thus increasing the total production cost of activated carbon.

There is a growing interest for researchers to convert renewable sources of agricultural wastes into adsorbent. Usually, these wastes are creating disposal problem due to the enormous demand of this fruit especially in Malaysia, the amount of its peel which poses no economic value and creating disposal problems to the community had increased too. Thus, an effort was done in this study to convert the durian peel (DP) into activated carbon to remove MG dye. Physicochemical activation approach comprising of heat treatment together with CO₂ gasification and KOH chemical treatment were employed in this study to create durian peel based AC (DPAC) with good adsorbent characteristic.

EXPERIMENTAL

Materials

Basic dye, MG used in this study as an adsorbate was obtained from Sigma-Aldrich (M) Malaysia. Its chemical formula is C₁₀H₇ClN₂O·HCl and its molecular weight is 382.93 g/mol. Deionized water used to prepare solutions was supplied by USF ELGA water treatment system. Its chemical formula is C₂H₂O₇·H₂O and its molecular weight is 382.93 g/mol.

Synthesis and characterization of DPAC

The DP collected locally in the area of Seberang Jaya, Penang, Malaysia was washed thoroughly to remove dirt on its surfaces. Clean DP was then subjected with dehydrating process at temperature of 110 °C by using an oven (Model Memmert 600, Germany), before being ground and sieved (size of 1-2 mm).

50 g of dried precursor was inserted in the center of the vertical tubular reactor and purging through the reactor was nitrogen gas that flows at 150 cm³/min. The temperature of the furnace was raise to 550 °C, then held constant for 1 hour. After that, the temperature of the reactor was let to decrease back to room temperature with nitrogen gas purging through the reactor still. The resulted char was collected from the reactor and was impregnated with chemical ativation agent, potassium hydroxide (KOH) at different impregnation ratio (IR), which can be computed using Eq. (1):

\[ IR = \frac{W_{KOH}}{W_{char}} \]  

where \( W_{KOH} \) and \( W_{char} \) represent the KOH pellets (dry weight) and char (dry weight), respectively. Char and KOH pellets were mixed together with deionized water using beaker of the size of 250 mL. The mixture was agitated and then kept in oven overnight (110 °C) for dehydrating purposes. Then, the sample was loaded inside the vertical tubular reactor once again, so that the activation step which is quite similar with carbonization process, could take place. This time, nitrogen gas was changed to carbon dioxide (CO₂) once the activation temperature was raised, at flow rate of 150 cm³/min and held for certain activation time. The reactor was then allowed to reach room temperature with nitrogen gas purging through it. Hot deionized water together with 0.1 M hydrochloric acid were used to wash the sample in order to recover excess KOH that attached to the sample. The aim in washing step is to obtain pH of washing solution between 6.5 and 7.

Samples was characterized by using surface area analyzer, scanning electron microscopy (SEM), simultaneous thermogravimetric analyzer (STA) and Fourier transform infrared spectroscopy (FTIR). Characterization of DPAC was made in terms of surface area, pore volume and average pore diameter by employing adsorption isotherm of nitrogen at temperature of 77 K by using surface area analyser (Micromeritics, Model ASAP 2020, USA). On the other hand, Brunauer-Emmett-Teller (BET) equation was employed to calculate DPAC’s BET surface area. SEM was used to study the surface morphology of the sample. The analysis was carried out using a SEM analyzer (Model Quanta 450 FEG, Netherlands). Proximate analysis of the sample was conducted using STA (Model Perkin Elmer STA 6000, USA) whereas the surface chemistry of the sample was measured using FTIR spectroscopy (Model IR Prestige 21 Shimadzu, Japan).

Adsorption studies

Batch equilibrium studies for MG-DPAC adsorption system was conducted by focusing on several important parameters namely, effect of MG initial concentration, effect of contact time between adsorbate and adsorbent, effect of MG solution temperature and lastly, effect of Mg solution pH. Accurately weighted 1.00 g of MG in powder form was mixed with 1000 mL deionized water to produce 1000 mg/L of stock solution. The sample solution was withdrawn at the point of equilibrium so that the residual concentration can be determined. UV-Visible spectrophotometer (Model Shidmadzu UV-1800, Japan) was used to measure the sample concentration at maximum wavelength of 615 nm. MG dye adsorbed at the point of equilibrium, \( q_e \) (mg/g) was computed according to Eq. (2) and MG percente removal was calculated as expressed in Eq. (3):

\[ q_e = \frac{C_0 - C_e}{W} \]  

\[ \% \text{ Removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \]

where \( C_0 \) and \( C_e \) are the MG dye concentration at initial and at equilibrium (mg/g), respectively, \( V \) is the volume of MG dye solution (ml) and \( W \) is the mass of DPAC (g).

200 mL of adsorbate solutions of pre-determined initial concentrations (25–300 mg/L) were created and filled in six Erlenmeyer flasks with a volume of 250 mL each. The mass of DPAC that was inserted in each flasks containing MG solution was fixed at 0.2 g. The flasks were covered with aluminium foil and loaded in an isothermal water bath shaker. The speed of the rotation for the water bath shaker was fixed at 120 rpm while its temperature was held constant at 30 °C. The process was continue until the MG concentration reading gave an indication that the equilibrium point has been reached. For this particular study, pH of MG solution was not altered.

To study the performance of MG-DPAC system under the influence of temperature, MG solution temperature was change from 30 to 45 and lastly, 60 °C. At these 3 different temperature conditions, parameters namely solution pH, rotating speed and dosage of DPAC were fixed at constant values.

Similarly, the pH of MG solution was change from pH 4 to 10 in order to study the adsorption performance of MG-DPAC system under the influence of pH. The alteration of pH of MG solution was made by the aid of 0.1 M HCl (hydrochloric acid) and/or 0.1 M NaOH (sodium hydroxide) and pH reading was obtained by using pH meter (Model Delta 320, Mettler Toledo, China). The parameters of initial MG concentration, adsorbent dosage and solution temperature were fixed at 50 mg/L, 0.2 g/200 mL and 30 °C, respectively.

In kinetic studies, relatively alike procedure as batch equilibrium studies was performed. However, the sample was taken out for reading
at preset time interval. Quantity of MG dye removed at time \( t \), \( q_t \) was computed using the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{W}
\]  

(4)

where \( C_0 \) and \( C_t \) are the MG dye concentration at initial and at time \( t \) (mg/g), respectively, \( V \) is the volume of MG dye solution (ml) and \( W \) is the mass of DPAC (g). The normalized standard deviation \( \Delta q_p(\%) \) for validation of kinetic model was calculated using (Weng et al., 2009):

\[
\Delta q_p(\%) = 100\sqrt{\frac{\sum{(q_{t,exp} - q_{t,cal})^2}}{(n-1)}}
\]

(5)

where \( n \) is data points while measured MG and calculated MG adsorbed at time \( t \) were denoted by \( q_{t,exp} \) and \( q_{t,cal} \), respectively.

RESULTS AND DISCUSSION

Characteristics of samples

The values of surface area (BET and mesopores) and pore characteristics (volume and diameter) for DP, DP char and DPAC were tabulated in Table 1. The surface area for DPAC was 886.31 m²/g whereas the surface area for DP was not available since there was no pore identified. Surface area obtained was considered average compared to ACs derived from Egyptian wood of 603 m²/g (Ilincic et al., 2020), durian seed of 980.62 m²/g (Ab Razak et al., 2015) and spent mushroom compost of 1419.11 m²/g (Karadirek and Okkay, 2018). The average pore diameter for DPAC was 2.57 nm which belong to mesopores region according to the IUPAC classification. KOH impregnation and CO₂ gasification applied during the activation steps had developed new pores and widening existing pores thus contributing to the surface area enhancement in DPAC. Dehydration of KOH produced K₂O which subsequently reacted with CO₂ to yield K₂CO₃, K₂CO₃ was mobile and penetrated deep into the DPAC’s skeleton and causing an increase to both surface area and pore volume.

Table 1 Surface area and pore characteristics of samples.

| Sample | BET surface area (m²/g) | Mesopore surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) |
|--------|------------------------|-----------------------------|--------------------------|---------------------------|
| DP     | 2.07                   | -                           | -                        | -                         |
| DP char| 177.64                 | 85.68                       | 0.17                     | 2.49                      |
| DPAC   | 886.31                 | 547.85                      | 0.50                     | 2.57                      |

Fig. 2 provides the morphology of DP and DPAC. The surface of DP (Fig. 2(a)) was rough with minimal existence of small size of pores. The surface of DPAC (Fig. 2(b)) was observed to be highly porous with cavities scattered irregularly across the whole surface. These heterogeneous cavities were resulted from the evaporation of impregnated KOH-derived compounds. Combination of CO₂ and KOH treatments were succeeded in aiding the well-development of pores on DPAC’s surface.

![Fig. 2 SEM images of (a) DP and (b) DPAC.](image)

Table 2 Proximate analysis of samples.

| Sample | Moisture (%) | Volatile (%) | Fixed carbon (%) | Ash (%) |
|--------|--------------|--------------|------------------|--------|
| DP     | 12.70        | 65.22        | 20.69            | 1.39   |
| DP char| 4.81         | 37.81        | 55.80            | 1.58   |
| DPAC   | 1.54         | 23.60        | 73.20            | 1.66   |

The surface chemistry of DP and DPAC is given in Fig. 3. It was observed that DP was having bandwidth at 3233 and 3459 cm⁻¹ (O-H functional group) (Ghaedi et al., 2015), 2351 cm⁻¹ (C=C stretching of alkyne group) (Georgin et al., 2016), 1647 cm⁻¹ (C=C alkene group) (Zhou et al., 2017), 1420 and 1498 cm⁻¹ (C-O stretching of ether) (Kumar and Jena, 2016), 1053 cm⁻¹ (carboxylic acid or ester group) (Gautam et al., 2015) and 616-825 cm⁻¹ (C-H out of plane bonding in benzene derivatives) (Lin et al., 2017). The surface chemistry of the DPAC was contradicted from its precursor since several functional groups had shifted or disappeared after the activation processes. Spectrum of DPAC shows that a few peaks located in the region of 2351 cm⁻¹ (C=C alkyne group) and 1647 cm⁻¹ (C=O alkene group) were diminished. It was noticed that the peaks in the region of 614-827 cm⁻¹ which signified CH out-of-plane bonding in benzene derivatives for DPAC was disappeared. Aromatic group diminished because of oxidative breakdown of benzene during pyrolysis and activation processes.

Batch equilibrium studies

Figs. 4 and 5 show the MG adsorption uptake and MG removal by DPAC at 30 °C, respectively. In the beginning, DPAC has excess surface sites which were available for the adsorption to occur. The amount of MG adsorbed together with the MG removal were found to rise with time until reached the equilibrium point. This point indicated that DPAC had become saturated, thus no more MG dye can be adsorbed. Plus, the repulsion that occur between MG dye in solid phase and bulk phase increase the difficulty of the remaining active sites on DPAC to be filled by MG dye. MG adsorption uptakes by DPAC was noticed to rise from 23.50 to 211.32 mg/g as the MG dye initial concentration increased from 25 to 300 mg/L. This was due to the occurrence of larger mass transfer driving force for higher MG
concentration, resulted in higher MG uptake. However, as the initial concentration of adsorbate was altered from 25 to 300 mg/L, the removal of MG decreased. The MG removal of higher than 84% was obtained for low initial concentration (25 to 100 mg/L) as the ratio of initial number of dye molecules to the accessible surface area was high.

The effect of uniformly distributed binding energies between adsorbent and adsorbate was high.

Fig. 6 illustrates the influence of initial pH on the MG adsorption by DPAC. The MG removal by DPAC was increased as the pH increased from 4 to 8. The highest removal was obtained at pH 8 of 90.63%, which proved that the MG adsorption was favor at alkaline condition. At acidic condition, the removal was low due to the existence of extra hydrogen ions competed with the MG ions for adsorption (Shakib et al., 2017). At higher pH, active sites with negative charge increased while active sites with positive charge decreased. This diminished the electrostatic repulsion between DPAC’s active sites and MG positive ions, thus resulted in an increased of MG adsorption uptakes.

Fig. 7 illustrates the influence of initial pH on the MG adsorption by DPAC. The MG removal by DPAC was increased as the pH increased from 4 to 8. The highest removal was obtained at pH 8 of 90.63%, which proved that the MG adsorption was favor at alkaline condition. At acidic condition, the removal was low due to the existence of extra hydrogen ions competed with the MG ions for adsorption (Shakib et al., 2017). At higher pH, active sites with negative charge increased while active sites with positive charge decreased. This diminished the electrostatic repulsion between DPAC’s active sites and MG positive ions, thus resulted in an increased of MG adsorption uptakes.

Fig. 7 MG removal by DPAC at different solution pH.

Isotherms studies provide valuable information about the relationship between adsorbate molecules in bulk phase and solid phase. In this study, eight isotherms were employed namely Langmuir, Freundlich, Temkin, Dubinin-Raduskevich (DR), Koble-Corrigan (KC), Vieth-Sladek (VS), Sips and Srebrou-Sotolongo (BS).

Langmuir isotherm was developed by assuming that the adsorbate formed a monolayer coverage on adsorbent’s surface. One of the most vital information can be obtained from this isotherm is the Langmuir monolayer adsorption capacity. The following equation gave the linear form of Langmuir isotherm (Langmuir, 1918):

$$q_e = \frac{q_m c_e}{1 + \frac{c_e}{q_m}}$$

where, $q_e$ is the quantity of MG dye removed at equilibrium (mg/g), $q_m$ is the monolayer adsorption capacity (mg/g), $C_e$ is the MG dye concentration at equilibrium (mg/L) and $K_L$ is the Langmuir adsorption constant (L/mg).

Freundlich isotherm was developed by assuming that the adsorbate formed a multilayer coverage on adsorbent’s heterogeneous surface and its linear form was expressed as follows (Freundlich, 1906):

$$\log q_e = \frac{1}{n_f} \log C_e + \log K_F$$

where, $q_e$ is the quantity of MG dye removed at equilibrium (mg/g), $C_e$ is the MG dye concentration at equilibrium (mg/L), $K_F$ is the Freundlich adsorption constant (mg/g)(L/mg)$^{1/n_f}$ and $n_f$ is the heterogeneity factor.

The equation of Temkin isotherm was built by considering the effect of solution temperature on MG adsorption. The adsorption uptakes were decreased as the solution temperature increased (Langmuir, 1918).

The decreasing trend in MG adsorption uptakes when temperature was increased was expected to be caused by the intensification of desorption step in the sorption mechanism (Doumic et al., 2015). This phenomenon was also contributed by the decrease in intensity of sorptive forces that occurred in MG-DPAC adsorption system.

Fig. 6 MG removal by DPAC at different solution temperature.

Fig. 4 MG adsorption uptake by DPAC versus the time at 30°C.

Fig. 5 MG percent removal by DPAC versus the time at 30°C.
obtained is in between of 8 and 16 kJ/mol, it signifies chemisorption. On the other hand, the value that below 8 kJ/mol indicates physisorption process. The equation of DR isotherm is expressed as follows (Dubinin and Radushkevich, 1947):

\[ q_e = q_m e^{-RTz} \]  \hspace{1cm}(9)

\[ e = RT \ln \left[ 1 + \frac{1}{C_e} \right] \]  \hspace{1cm}(10)

Free energy \( E_{DR} \) of sorption was calculated as follows:

\[ E_{DR} = \frac{1}{V_{DR}} \]  \hspace{1cm}(11)

where \( q_e \) is the quantity of MG dye removed at equilibrium (mg/g), \( q_m \) is the monolayer adsorption capacity (mg/g), \( C_e \) is the MG dye concentration at equilibrium (mg/L), \( T \) is absolute temperature (K), \( R \) is the universal gas constant (8.314 J/mol K) and \( B_{DR} \) is DR constant.

Isotherm model of Koble-Corriigan (KC) is an empirical model with 3 parameters. This model is given by following equation (Koble and Corriigan, 1952):

\[ q_e = \frac{a_{KC}C_e^{m_C}}{1 + a_{KC}C_e^{m_C}} \]  \hspace{1cm}(12)

where \( q_e \) is the quantity of MG dye removed at equilibrium (mg/g), \( C_e \) is the MG dye concentration at equilibrium (mg/L) and \( a_{KC}, m_C, n_C \) are the KC parameters. If the value of parameter \( n_C \) is close to 1, it signifies that the isotherm is becoming more of Langmuir isotherm.

The Vieth-Sladek (VS) isotherm equation is given as follows (Vieth and Sladek, 1965):

\[ q_e = k_{VS}C_e + \frac{q_m \beta_{VS}C_e}{1 + \beta_{VS}C_e} \]  \hspace{1cm}(13)

where \( q_e \) is the quantity of MG dye removed at equilibrium (mg/g), \( C_e \) is the MG dye concentration at equilibrium (mg/L) and \( k_{VS} \) and \( \beta_{VS} \) are VS constants.

Sips isotherm equation is given as (Sips, 1948):

\[ q_e = \frac{q_m(k_C C_e)^n}{1 + (k_C C_e)^n} \]  \hspace{1cm}(14)

where \( q_e \) is the quantity of MG dye removed at equilibrium (mg/g) and \( C_e \) is the MG dye concentration at equilibrium (mg/L) and \( q_m, k_C, n_C \) and \( n_S \) are Sips parameters. When \( n_S \) equals to unity, the Sips isotherm becomes Langmuir isotherm. On the other hand, deviation of \( n_S \) value from unity indicates heterogeneous surface.

The Brouers-Sotolongo (BS) isotherm is given by (Gregg and Sing, 1967):

\[ q_e = q_m \left( 1 - e^{-k_{BS}C_e} \right) \]  \hspace{1cm}(15)

where \( q_e \) is the quantity of MG dye removed at equilibrium (mg/g), \( C_e \) is the MG dye concentration at equilibrium (mg/L) and \( k_{BS}, \alpha \) and \( q_m \) are BS parameters. The parameters \( q_m, k_{BS} \) and \( \alpha \) can be determined by a non-linear curve fitting procedure. The exponent \( \alpha \) signifies the energy heterogeneity of the surface of adsorbent.

The summary of the isotherm constants for MG-DPAC adsorption system were given in Table 3. Comparison on \( R^2 \) values revealed that adsorption data matched the isotherm models in the sequence of Freundlich > Langmuir > Temkin > KC > BS > Sips > VS > DR. Freundlich isotherm fitted well with the data (\( R^2 > 0.99 \)), which signifies that a multilayer sorption was occurred at DPAC’s heterogeneous surface. The values of \( n_F \) was 3.06 which indicative of high adsorption intensity (Tunc et al., 2009). The heterogeneity in the surface of the DPAC significantly affect the MG adsorption. The high \( K_F \) values of 19.08 indicate the higher adsorption capacity. Freundlich isotherm was preferred by other studies of basic blue removal by pineapple plant stem based AC (Chan et al., 2016). The maximum monolayer capacity, \( q_m \) values from the models obtained were in range 231.17 to 241.66 mg/g.

| Parameters of isotherms. | Langmuir | Freundlich | Temkin | Dubinin-Radushkevich |
|--------------------------|----------|------------|--------|-----------------------|
| \( q_m \) = 231.17       | \( K_F \) = 19.08 | \( B_T \) = 46.73 | \( E_{DR} \) = 2236.07 |
| \( k_L \) = 0.11         | \( n_F \) = 3.06 | \( A_T \) = 0.06 | \( B_{DR} \) = 0.0070 |
| \( R^2 \) = 0.98         | \( R^2 \) = 0.99 | \( R^2 \) = 0.94 | \( R^2 \) = 0.72     |

Additional analysis of the Langmuir isotherm can be computed by using the following equation to find separation factor, \( R_L \):

\[ R_L = \frac{1}{1 + k_L C_0} \]  \hspace{1cm}(16)

where \( C_0 \) is the initial concentration of MG dye (mg/L). Different value of \( R_L \) indicates different condition: \( 0 < R_L < 1 \) indicates favourable adsorption, \( R_L > 1 \) indicates unfavourable adsorption, \( R_L = 1 \) indicates linear adsorption and \( R_L = 0 \) indicates irreversible adsorption. Fig. 8 shows the graph of \( R_L \) versus MG initial concentrations. From Fig. 9, it can be seen that \( R_L \) values obtained were in favorable region. As the initial concentration rises from 25 to 300 mg/L, a gradual drop of \( R_L \) was spotted, which signified that adsorption process at higher initial MG dye concentration was preferred.

### Adsorption kinetics

Kinetic studies provides the rate of reaction for adsorption process. This study employed 4 kinetic models namely, pseudo-first-order (PFO) model, pseudo-second-order (PSO) model, Elovich model and Avrami model.

The pseudo-first-order (PFO) model is given as (Lagergren and Svenska, 1898):

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  \hspace{1cm}(17)

where \( q_t \) and \( q_e \) are the quantity of MG dye removed at equilibrium and at time \( t \) (mg/g), respectively, \( k_1 \) is the rate constant for PFO model (1/min) and \( t \) is time (min).

Equation for pseudo-second-order (PSO) model is given as follows (Ho and Mckay, 1999):

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm}(18)

where \( q_t \) and \( q_e \) are the quantity of MG dye removed at equilibrium and at time \( t \) (mg/g), respectively, \( k_2 \) is the rate constant for PSO model (g/mg h) and \( t \) is time (min).

Equation of Elovich kinetic model is as follows (Aharoni and Tompkins, 1970):

\[ q_t = q_m (1 - e^{-k_3 t}) \]  \hspace{1cm}(19)

where \( q_t \) and \( q_e \) are the quantity of MG dye removed at equilibrium and at time \( t \) (mg/g), respectively, \( k_3 \) is the rate constant for Elovich model (mg/g h) and \( t \) is time (min).
where \( q_t \) is the MG dye adsorbed at time \( t \) (mg/g), \( A \) is the rate of initial sorption (mg/g h), \( B \) is the parameter related to surface coverage extension (g/mg) and \( 1/B \) reflects the numbers of sites available for adsorption.

Avrami kinetic model is given as (Putniss, 1995):

\[
q_t = q_e \left(1 - \exp\left(-k_{Av}t^n\right)\right)
\]  
(20)

In simpler form, this equation becomes:

\[
\alpha_t = \left(1 - \exp\left(-k_{Av}t^n\right)\right)
\]  
(21)

The linearized form of this equation is:

\[
\ln(-\ln(1 - \alpha_t)) = \ln(k_{Av} + n_{AV}\ln t)
\]  
(22)

where \( q_e \) and \( q_t \) are the quantity of MG dye removed at equilibrium and at time \( t \) (mg/g), respectively, \( k_{Av} \) is the Avrami constant, \( n_{AV} \) is the constant that reflects the adsorption mechanism changes and \( \alpha_t \) is the adsorption fraction of \( q_t/q_e \). Table 4 shows the kinetic parameters for the MG adsorption onto DPAC. Based on Table 4, PFO kinetic model was revealed to match the data the best as shown by the highest \( R^2 \) values with small standard deviation, \( \Delta q_p \). Furthermore, the values of \( q_e \) calculated using PFO equation is comparable to those obtained from the experiment which resulted \( \Delta q_p \) to be ranging from 0.69 to 8.50 %.

Table 4 Kinetic parameters for MG adsorption onto DPAC.

| P  | 25 | 50 | 100 | 200 | 250 | 300 |
|---|---|---|---|---|---|---|
| MG initial concentration (mg/L) |
| q_e, exp (mg/g) | 23.35 | 46.34 | 85.83 | 138.40 | 163.69 | 172.43 |
| E | 5 | 0.85 | 0.70 | 0.53 | 0.51 | 0.49 | 0.47 |
| R^2 | 0.99 | 0.98 | 0.99 | 0.95 | 0.97 | 0.96 |
| \( \Delta q_p \) (%) | 4.47 | 8.50 | 6.69 | 4.08 | 2.64 | 7.50 |

The next section where the rate limiting step is caused by intraparticle diffusion is known as gradual adsorption. The third section which is known as final equilibrium stage signifies a drop in intraparticle diffusion because of exceptionally low MG dye concentration left in the solution. It can be concluded that intraparticle diffusion was not the only rate-limiting step in the second and third sections since the linear lines do not pass through the origin. Table 5 tabulates the values of the intraparticle diffusion model constants (\( k_p \) and \( C \)) for the three regions from the plots of \( q_e \) versus \( t^{1/2} \) together with the \( R^2 \) values. From Table 5, it can be seen that \( k_p \) for all sections increased with the increased of initial dye concentrations. The explanation behind this is that an increasing in adsorbate concentration caused the driving force to increase, thus lead to an increase in the MG diffusion rate. Besides \( k_p \), \( C \) was also found to increase as the MG initial concentrations increase which indicates an increase of the boundary layer thickness and increase of the chance of internal mass transfer (Marrakchi et al., 2017).

Boyd kinetic model is applied to decide the slowest step in the adsorption process, as described in (Boyd et al., 1947):

\[
B_t = -0.4977 - \ln \left(1 - \frac{q_t}{q_e}\right)
\]  
(24)

where \( q_e \) and \( q_t \) are the quantity of MG dye removed at equilibrium and at time \( t \) (mg/g), respectively. Fig. 10 illustrates the Boyd plots and from the plot, the linear lines did not passing through the origin, for all MG initial concentrations. Therefore, it can be said that the adsorption of MG dye onto DPAC was mainly regulated by the processes that were managed by film diffusion.

Thermodynamic studies

Three important parameters in thermodynamic studies; enthalpy of adsorption (\( \Delta H^o \)), free energy (\( \Delta G^o \)) and entropy (\( \Delta S^o \)) were discovered and given in Table 5 together with activation energy value, \( E_a \). The value of \( \Delta H^o \) and \( \Delta S^o \) can be obtained from equation given below:

\[
\ln K_e = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]  
(25)

The next following equation can be applied to obtain the value of \( \Delta G^o \) is:

\[
\Delta G^o = -RT\ln K_e
\]  
(26)

The mechanism of MG diffusion was investigated by using Intraparticle diffusion and Boyd models. Intraparticle diffusion model is usual to majority of adsorption process where the uptake of adsorbate differs nearly proportional with \( t^{1/2} \). The equation of this model expressed as (Weber and Morris, 1962):

\[
q_t = k_{diff}t^{1/2} + C
\]  
(23)
where $R$ is the universal gas constant (8.314 J/mol K), $T$ is absolute solution temperature (K) and $K_L$ is the Langmuir isotherm constant (L/mg). Activation energy of adsorption refers to the lowest energy which is required by reactant for the reaction to progress. This energy can be determined by employing Arrhenius equation which is given as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$

where $k_2$ is the rate constant of PSO model (g/mg h), $E_a$ is the Arrhenius activation energy of adsorption (kJ/mol), $A$ is the Arrhenius factor, $R$ is the universal gas constant (8.314 J/mol K) and $T$ is the absolute temperature (K). From Table 5, negative value of $\Delta H^*$ signifies nature of exothermic process. This result was in agreement with those results obtained in effect of solution temperature section in 3.3. Exothermic nature occurs due to the fact that physical bonding between MG dye and DPAC’s active sites got reduced as temperature increased. Apart from that, solubility of MG dye was enhanced owing to a greater interaction forces between MG dye and water as compared to a weaker interaction forces between MG dye and DPAC, hence the solute was more difficult to be adsorbed. Exothermic nature can be observed in the studies of Basic Blue 3 adsorption onto pineapple plant stem based AC (Chan et al., 2016). The negative value of $\Delta S^*$ suggest the decrease in adsorbate concentration in solid-liquid interface, which signified that there is an increase in adsorbate concentration onto the solid phase. It can also be deduced that the randomness at the solid-liquid interface had decreased during adsorption process. This phenomenon is common for physical-type of adsorption where the adsorption process was driven by electrostatic interaction.

Low activation energy between 5–40 kJ/mol indicates physical adsorption. On contrary, energy between 40–80 kJ/mol proposes chemisorption. Activation energy, $E_a$ for MG-DPAC system was found to be positive and below than 40 kJ/mol, thus indicated that the rate limiting step was physically control type. $\Delta G^*$ with negative values as obtained in this study signified that MG-DPAC adsorption process had a spontaneous and feasible nature. Table 6 shows the summary of other AC adsorbents in adsorbing MG dye.

CONCLUSION

In this study, the adsorption of MG dye onto DPAC was increased with the increase of contact time and dye initial concentration. The adsorption system poses exothermic nature as the adsorption uptake was decreased as the solution temperature increased. pH 8 was found to be the optimum pH for the MG dye adsorption onto DPAC. Isotherm and kinetic studies revealed that Freundlich isotherm and PFO kinetic model fit the data the best. Further analysis using Boyd plot confirmed that adsorption of MG onto DPAC was mainly governed by the film diffusion controlled mechanism. Thermodynamic studies revealed low value of activation energy, $E_a$ which indicates that the rate-limiting step in MG adsorption was physically control type. DPAC was found to be suitable to remove MG dye from aqueous solution due to high maximum adsorption capacity that it poses.

| Precondition | Adsorption capacity (mg/g) | Isotherm | Kinetic | Thermodynamic | References |
|--------------|---------------------------|---------|---------|---------------|------------|
| Algae       | 231.17                    | Freundlich | PFO | Exothermic | This study |
| Pinus       | 250.00                    | Langmuir | PSO | -             |            |
| Apple       | 706.72                    | Liu      | General | Exothermic |            |
| Cetraria     | 666.22                    | Freundlich | PSO | Endothermic |            |
| Spent      | 2.55                      | Langmuir | PSO | Exothermic |            |
| Walnut     | 11.76                     | Langmuir | PSO | -            |            |
| Coffee      | 263.00                    | Sips     | PSO | Endothermic |            |
| Luffa       | 78.79                     | Langmuir | PSO | Endothermic |            |
| Chrysopogon | 128.10                    | Freundlich | PSO | -            |            |

Table 6 Summary of other AC adsorbents in adsorbing MG dye.

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REFERENCES

Ab Razak, N. H., Praveena, S. M., Aris, A. Z., Hashim, Z. 2015. Drinking water studies: A review on heavy metal, application of biomarker and health risk assessment (A Special Focus In Malaysia). J. Epidemiol. Glob. Health, 5, 297-310.

Adebowo, M. A., Adebomi, J. I., Abe, T. O., Areo, F. I. 2020. Removal of aqueous congo red and malachite green using acake apple seed–bentonite composite. Colloid Interface. Sci. Commun., 38, 100311.

Aderemi, H. B., Nasri, N. S., Zainia, M. A. A. 2018. Physicochemical properties of char derived from palm fatty acid distillate. Mal. J. Fund. Appl. Sci., 14, 1013-406.

Aharoni, C., Tompkins, F. C. 1970. Advances in catalysis and related subjects. Academic Press, 31.

Ahmad, M. A., Ahmad, N., Bello, O. S. 2015. Adsorption kinetic studies for the removal of synthetic dye using durian seed activated carbon. J. Dispers. Sci. Technol., 36, 670-684.

Aldaihi, T. M., Abustan, I., Ahmad, M. A., Abu Foul, A. 2015. Comparative studies on the olive stone activated carbon adsorption of Zn²⁺, Ni²⁺, and Cd²⁺ from synthetic wastewater. Desalination Water Treat., 54, 166-177.

Ayanda, O. S., Adiogho, O. E., Olutona, G. O., Abubaker, O. T., Nelnia, S. M., Naidoo, E. B. 2018. Effectiveness of termite hill as an economic adsorbent for the adsorption of alizarin red dye. J. Water Resuse Desalination, 9, 83-93.

Aziz, N. S. M., Shariff, A., Abdullah, N., Noor, N. M. 2018. Characteristics of coconut frond as a potential feedstock for biochar via slow pyrolysis. Mal. J. Fund. Appl. Sci., 14, 408-413.

Bahadori, E., Rapf, M., Di Michele, A., Rossetti, I. 2020. Photochemical vs photocatalytic azo-dye removal in a pilot free-surface reactor: is the catalyst effective? Sep. Purif. Technol., 237, 116320.

Bai, Y.-N., Wang, X.-N., Zhang, F., Wu, J., Zhang, W., Lu, Y.-Z., Fu, L., Lau, T.-C., Zeng, R. J. 2020. High-rate anaerobic decolorization of methyl orange
from synthetic azo dye wastewater in a methanobased hollow fiber membrane bioreactor. J. Hazard. Mater., 388, 121753.

Berkessa, Y. W., Yan, L., T., Jagatheesan, V., Zhang, Y. 2020. Treatment of anthraquinone dye textile wastewater using anaerobic dynamic membrane bioreactor: performance and microbial dynamics. Chemosphere, 238, 124539.

Bhatti, H. N., Jabeen, A., Iqbal, M., Noreen, S., Naseem, Z. 2017. Adsorptive behavior of rice bran-based composites for malachite green dye: isotherm, kinetic and thermodynamic studies. J. Mol. Liq., 237, 322-333.

Boyd, G. E., Adamson, A. W., Myers, L. S. 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites II. J. Am. Chem. Soc., 69, 11, 2836-2848.

Chan, S.-L., Tan, Y. P., Abdullah, A. H., Ong, S.-T. 2016. Equilibrium, kinetic and thermodynamic studies of a new potential biosorbent for the removal of basic blue 3 and congo red dyes: pineapple (ananas comosus) plant stem. J. Taiwan Inst. Chem. Eng., 61, 306-315.

Chanzu, H. A., Onyari, J. M., Shindu, P. M. 2019. Brewers’ spent grain in adsorption of aqueous congo red and malachite green dyes: batch and continuous flow systems. J. Hazard. Mater., 380, 120897.

Douvnic, L., Salieri, G., Cassanello, M., Haure, P., Ayude, M. 2015. Efficient removal of orange g using prussian blue nanoparticles supported over alumina. Catal. Today, 240, 67-72.

Dubinin, M. M., Radushkevich, L. V. 1947. The equation of the characteristic curve of activated charcoal. Proc. USSR Acad. Sci.: Physical Chemistry Section, 65, 133-137.

Eltaweel, A. S., Elgarhy, G. S., El-Sabrouti, G. M., Omr, A. M. 2020. Carboxyethyl cellulose/carboxylated graphene oxide composite microbeads for efficient adsorption of cationic methylene blue dye. Int. J. Biol. Macromol., 154, 348-358.

Farnane, M., Tounsi, H., Machrouhi, A., Elhalbi, A., Mahjoubi, F. Z., Saqdi, M., Abdennouri, M., Qurzal, S., Barka, N. 2017. Dye removal from aqueous solution by raw maize corncob and H2O2 activated maize corncob. J. Water Reuse Desalinization, 8, 214-224.

Freundlich, H. M. F. 1906. Over adsorption in solution. J. Phys. Chem., 57, 385-483.

Gautam, R. K., Gautam, P. K., Banerjee, S., rawat, V., Soni, S., Sharma, S. K., Chattopadhyay, M. C. 2015. Removal of trace metal by activated carbon from peanut shell by conventional pyrolysis and microwave assisted pyrolysis with chemical activation, an effective adsorbent for the removal of malachite green from aqueous solution. J. Mol. Liq., 274, 315-327.

Hameed, B. H. 2017. Microwave assisted pyrolysis with chemical activation, an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent. J. Clean. Prod., 162, 1376-1387.

Ho, Y. S., Nasar, A. 2019. Preparation, characterization and adsorption studies of the chemically modified luffa aegyptica peat as a potential adsorbent for the removal of malachite green from aqueous solution. J. Mol. Liq., 274, 315-327.

Hough, P. N. Y., Ma, N. L., Lee, C. L., Chase, J. A., M., Yek, P. N. Y., M., Yek, P. N. Y., Ma, N. L., Lee, C. L., Chase, J. A., M., Yek, P. N. Y. 2018. The green dispersion of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40, 1361.

In, Q., Gao, M., Chang, J., Ma, H. 2017. Highly effective adsorption performance of carboxymethyl cellulose microspheres crosslinked with epichlorohydrin. J. Appl. Polym. Sci., 2, 134.

Jung, J. H., Park, S., Park, J., Park, S., Park, J. 2010. Electrochemical degradation of methylene blue from sludge using electrochemically synthesized boron doped diamond/carbon fiber composite as anode in glassy polymer. Journal Of Colloid Science, 20, 1014-1033.

Kumar, A., Jena, H. M. 2016. Preparation and characterization of high surface area activated carbon from fox nut (euryale ferox) shell by chemical activation with H2O2. Results Phys., 6, 651-658.

Langmuir, I. 1918. The theory of adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40, 1361.

Lin, Q., Gao, M., Chang, J., Ma, H. 2017. Highly effective adsorption performance of carboxymethyl cellulose microspheres crosslinked with epichlorohydrin. J. Appl. Polym. Sci., 2, 134.

Mota, H. P., Quadrado, R. F. N., Burgo, T. A. L., Iglesias, B. A., Fajardo, A. R. 2020. Polysaccharide/Fe(III)-porphyrin hybrid film as catalyst for oxidative decolorization of toxic azo dyes: An approach for wastewater treatment. Arab. J. Chem., 13, 7, 5923-5938.

Noor, N. M., Sharifir, A., Abdollahi, N., Aziz, N. S. M. 2019. Temperature effect on biochar properties from slow pyrolysis of coconut flesh waste. Mal. J. Fund. Appl. Sci., 15, 153-158.

Pereira, L. A., Couto, A. B., Almeida, D. A. L., Ferreira, N. G. 2020. Singular properties of boron-doped diamond/carbon fiber composite as anode in brilliant green dye electrochemical degradation. Diam. Relat. Mater., 103, 107708.

Putnis, A. 1995. Introduction To Mineral Sciences. Cambridge University Press, Melbourne.

Rahim, A. R. A., Kuanasean, K., Shelzad, N., Rabat, N. E., Johari, K., Mat, H. 2019. Synthesis and characterization of coconut pith char adsorbents for the removal of malachite green dye. J. Water Process Eng., 32, 100931.

Shibahara, T., Iwahashi, A., Kusama, K., Tomura, T. 2005. Adsorption of malachite green dye by using chitosan-g-tiaconic acid/bentonite nanocomposite – equilibrium and kinetic study. Water Sci. Technol., 75, 1932-1943.

Shimzuddin, M. S., Yussuf, N. N. N., Sulaiman, M. A. 2016. Synthesis and characterization of activated carbon produced from kenaf core fiber using H2O2 activation. Procedia Chem., 19, 558-565.

Sharma, G., Sharma, S., Kurnar, A., Naushad, M., Du, B., Ahamad, T., Ghiar, A. A., Alqadami, A. A. J., Stadler, F. 2019. Honeycomb structured activated carbon synthesized from pinus roxburghii cone as effective biosorbent for toxic malachite green dye. J. Water Process Eng., 32, 100931.

Sips, R. 1948. Combined form of Langmuir and Freundlich equations. J. Chem. Phys., 16, 490-495.

Temkín, M. I., Pyszhe, V. 1940. Kinetics of ammonia synthesis on promoted iron catalyst. Acta Physchimica U.S.S.R., 12, 327-356.

Thanarasu, A., Periyasamy, K., Manickam Periyaraman, P., Devaraj, T., Velayutham, K., Subramanian, S. 2020. Comparative studies on adsorption of dye and heavy metal ions from effluents using eco-friendly adsorbent. Mater. Today. In press.

Tunc, O., Tanac, H., Aksu, Z. 2009. Potential use of cotton plant wastes for the removal of remozol black reactive dye. J. Hazard. Mater., 163, 187-198.

Vega-Negron, A. L., Alamo-Nole, L., Perales-Perez, O., Gonzalez-Mederos, A. M., Jusino-Olivencia, C., Roman-Velazquez, F. R. 2018. Simultaneous adsorption of cationic and anionic dyes by chitosan/cellulose beads for wastewaters treatment. Int. J. Environ. Res., 12, 59-65.

Wei, H., Sladek, K. J. 1965. A model for diffusion in glassy polymer. J. Water Process Eng., 21, 986-993.

Wen, C. H., Lin, Y. T., Tszeng, T. W. 2009. Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder. J. Hazard. Mater., 163, 187-198.

Zhou, L., Yu, Q., Cui, Y., Xie, F., Li, W., Li, Y., Chen, M. 2017. Adsorption properties of activated carbon from reed with a high adsorption capacity. Ecol. Eng., 102, 443-450.

Zhou, X., Zhang, J., Pan, Z., Li, D. 2019. Review of methods for the detection and determination of malachite green and leuco-malachite green in aquaculture. Crit. Rev. Anal. Chem., 49, 1-20.
Zhu, M., Yin, X., Chen, W., Yi, Z., Tian, H. 2018. Removal of sulphate from mine waters by electrocoagulation/rice straw activated carbon adsorption coupling in a batch system: optimization of process via response surface methodology. *J. Water Reuse Desal.*, 9, 163-172.

Zhu, Y., Wang, W., Ni, J., Hu, B. 2020. Cultivation of granules containing anaerobic decolorization and aerobic degradation cultures for the complete mineralization of azo dyes in wastewater. *Chemosphere*, 246, 125753.