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

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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 (Aderemi 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, modified nylons, 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 their limitation in application (Aziz et al., 2018). Examples of agricultural wastes include rice straw (Zhu et al., 2018), kernel shell (Zhi and Zaini, 2019), coconut pith (Rahim et al., 2019), coconut flesh waste (Noor et al., 2019), maize corn cob (Farnane et al., 2017), olive stone (Alsibi et al., 2015) and African palm shell (Moreno-Marencio et al., 2020). In this study, durian (Duriozibethinus L.) peel is selected to be converted into activated carbon. Durian is a tropical fruit that can be easily found in Malaysia and other Southeast Asia countries. 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 C₂₃H₂₃N₂O·HCl and its molecular weight is 382.93 g/mol. Deionized water used to prepare solutions was supplied by USF ELGA water treatment system. The structural formula of MG is given in Fig. 1.

![Chemical structure of MG dye](image)

**Fig. 1 Chemical structure of MG dye**

**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 activation 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 reached, 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 analyzer (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, Netherland). Approximate 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 Shimadzu 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 percent removal was calculated as expressed in Eq. (3):

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

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

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:

\[
q_t = \frac{(C_0 - C_1)W}{w}
\]

(4)

where \( C_0 \) and \( C_1 \) 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 \( \Delta q \) (%) for validation of kinetic model was calculated using (Weng et al., 2009):

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

(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 Okmay, 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Mesopore surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>2.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DP char</td>
<td>177.64</td>
<td>85.68</td>
<td>0.17</td>
<td>2.49</td>
</tr>
<tr>
<td>DPAC</td>
<td>886.31</td>
<td>547.85</td>
<td>0.50</td>
<td>2.57</td>
</tr>
</tbody>
</table>

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 heterogenous cavities were resulted from the evaporation of impregnated KOH-derived compounds. Combination of CO₂ and KOH treatments were succeed in aiding the well-development of pores on DPAC’s surface.

Proximate analysis for samples is tabulated in Table 2. DP contains 20.69 % of fixed carbon which can be considered moderate and suitable to be converted to AC at the first place. Other agricultural wastes contained wide range of fixed carbon from 11 % of kenaf fiber (Shamsuddin et al., 2016) to 34.80 % of orange peel (Lam et al., 2017). After activation processes, DPAC showed a significant increase in fixed carbon and a drastic decreased in volatile composition. At high activation temperature, most of the volatile and moisture were removed from the sample and leave behind high carbon content.

Table 2 Proximate analysis of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (%)</th>
<th>Proximate analysis (%)</th>
<th>Fixed carbon (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>12.70</td>
<td>65.22</td>
<td>20.69</td>
<td>1.39</td>
</tr>
<tr>
<td>DP char</td>
<td>4.81</td>
<td>37.81</td>
<td>55.80</td>
<td>1.58</td>
</tr>
<tr>
<td>DPAC</td>
<td>1.54</td>
<td>23.60</td>
<td>73.20</td>
<td>1.66</td>
</tr>
</tbody>
</table>

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 alkenes 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 alkyn group) and 1647 cm⁻¹ (C=C alkenes group) were diminished. It was noticed that the peaks in the region of 614-827 cm⁻¹ which signified C=H 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 uptake 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.

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.

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-Radushkevich (DR), Koble-Corrigan (KC), Vieth-Sladek (VS), Sips and Brouers-Sotolongo (BS). Langmuir isotherm was developed by assuming 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):

$$\frac{C_e}{q_e} = \frac{C_m}{q_m} + \frac{1}{n_q q_m}$$

(6)

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):

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

(7)

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 uniformly distributed binding energies between adsorbent and adsorbate. It is assumed that the heat of adsorption would dropped linearly with adsorbate’s coverage on adsorbent. Simplified linear equation of Temkin isotherm is expressed as follows (Temkin and Pyzhev, 1940):

$$q_e = B_T \ln A_T + B_T \ln C_e$$

(8)

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), $T$ is the absolute temperature (K), $R$ is the universal gas constant (8.314 J/mol.K), $A_T$ is the equilibrium binding constant (L/mg) and $B_T$ is the constant which related to the adsorption heat (L/mg).

DR isotherm estimates the characteristic porosity of the adsorbent, plus with adsorption’s apparent energy. When the free energy, $E_{DR}$
obtained is between 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):

\[ q_e = \frac{a_{KC} C_e}{1 + b_{KC} C_e^m} \]  
(9)

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

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

\[ E_{DR} = \frac{1}{\sqrt{2} R T} \]  
(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-Corrigan (KC) is an empirical model with 3 parameters. This model is given by following equation (Koble and Corrigan, 1952):

\[ q_e = \frac{a_{KC} C_e}{1 + b_{KC} C_e^m} \]  
(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 \( a_{KC}, b_{KC} \) and \( n_{KC} \) are the KC parameters. If the value of parameter \( n_{KC} \) 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):

\[ q_e = k_{VS} C_e + \frac{q_m p_{VS} C_e^m}{1 + p_{VS} C_e^m} \]  
(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/g), \( C_e \) is the MG dye concentration at equilibrium (mg/L) and \( k_{VS} \) and \( p_{VS} \) are VS constants.

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

\[ q_e = \frac{q_m (k C_e)^{\alpha}}{(k C_e)^{\alpha} + n_{S}} \]  
(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 \( k_{S}, \alpha \) 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):

\[ q_e = q_m \left(1 - e^{-k_{BS} C_e^\alpha} \right) \]  
(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.

### Table 3 Parameters of isotherms.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
<th>Dubinin-Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m )</td>
<td>231.17</td>
<td>19.08</td>
<td>46.73</td>
<td>2236.07</td>
</tr>
<tr>
<td>( k_l )</td>
<td>0.11</td>
<td>3.06</td>
<td>0.06</td>
<td>0.0070</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.98</td>
<td>0.99</td>
<td>0.94</td>
<td>0.72</td>
</tr>
</tbody>
</table>

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

\[ R_L = \frac{1}{1 + K_L C_0} \]  
(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, \( R_L = 0 \) indicates linear adsorption and \( R_L = \infty \) indicates irreversible adsorption. Fig. 8 shows the graph of the \( R_L \) 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):

\[ \ln q_t - q_e = -k_1 t \]  
(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):

\[ \frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \]  
(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):
where \( q_e \) 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 number of sites available for adsorption.

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

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

(20)

In simpler form, this equation becomes:

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

(21)

The linearized form of this equation is:

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

(22)

where \( q_t \) and \( q_i \) 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 \( q_t/q_i \). 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 shown by the highest \( R^2 \) values with small standard deviation, \( \Delta q_e \). Furthermore, the values of \( q_t \) calculated using PFO equation is comparable to those obtained from the experiment which resulted \( \Delta q_e \) to be ranging from 0.69 to 8.50%.

Table 4 Kinetic parameters for MG adsorption onto DPAC.

<table>
<thead>
<tr>
<th>P</th>
<th>MG initial concentration (mg/L)</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>q, exp</td>
<td>24.70</td>
<td>28.08</td>
<td>36.23</td>
<td>44.29</td>
<td>55.15</td>
<td>66.42</td>
</tr>
<tr>
<td>O</td>
<td>q, cal</td>
<td>23.35</td>
<td>44.54</td>
<td>85.63</td>
<td>138.40</td>
<td>163.69</td>
<td>172.43</td>
</tr>
<tr>
<td>S</td>
<td>k, cal</td>
<td>0.85</td>
<td>0.70</td>
<td>0.53</td>
<td>0.51</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td>E</td>
<td>R</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>0.95</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>P</td>
<td>q, cal</td>
<td>37.04</td>
<td>71.43</td>
<td>142.86</td>
<td>225.56</td>
<td>275.72</td>
<td>313.42</td>
</tr>
<tr>
<td>O</td>
<td>k, cal</td>
<td>0.017</td>
<td>0.0085</td>
<td>0.0023</td>
<td>0.0028</td>
<td>0.0029</td>
<td>0.0030</td>
</tr>
<tr>
<td>S</td>
<td>R</td>
<td>0.91</td>
<td>0.91</td>
<td>0.98</td>
<td>0.84</td>
<td>0.60</td>
<td>0.64</td>
</tr>
<tr>
<td>E</td>
<td>( \Delta q_e ) (%)</td>
<td>49.96</td>
<td>46.73</td>
<td>65.67</td>
<td>56.32</td>
<td>63.99</td>
<td>88.13</td>
</tr>
</tbody>
</table>

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

(24)

where \( q_e \) and \( q_i \) 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.

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:

\[
\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

(25)

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

\[
\Delta G^o = -RT \ln K_c
\]

(26)
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 required for the reaction to progress. This energy can be determined by employing Arrhenius equation which is given as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (27)

where $k_2$ is the rate constant of PSO model (g/mg h), $A$ is the Arrhenius activation energy of adsorption (kJ/mol), $E_a$ 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 $\Delta H^0$ signified 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 $\Delta S^0$ 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. $\Delta G^0$ 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.

### Table 5 Thermodynamic parameters for MG adsorption onto DPAC.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/mol)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-30.15</td>
<td>-0.12</td>
<td>29.94</td>
<td>-1.19</td>
</tr>
<tr>
<td>318</td>
<td>318K</td>
<td>-0.73</td>
<td>-0.28</td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>333K</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 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 uptakes 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.

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

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Adsorption capacity (mg/g)</th>
<th>Isotherm</th>
<th>Kinetic</th>
<th>Thermodynamic</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durian peel</td>
<td>231.17</td>
<td>Freundlich</td>
<td>PFO</td>
<td>Exothermic</td>
<td>This study</td>
</tr>
<tr>
<td>Pinus rusticulifera cone seed</td>
<td>250.00</td>
<td>Langmuir</td>
<td>PSO</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Apple seed</td>
<td>706.72</td>
<td>Liu</td>
<td>General order model</td>
<td>Exothermic</td>
<td></td>
</tr>
<tr>
<td>Lichen</td>
<td>666.22</td>
<td>Freundlich</td>
<td>PSO</td>
<td>Endothermic</td>
<td></td>
</tr>
<tr>
<td>Cetraria islandica Spent grain Walnut shell</td>
<td>2.55</td>
<td>Langmuir</td>
<td>PSO</td>
<td>Exothermic</td>
<td></td>
</tr>
<tr>
<td>Coffee husk</td>
<td>263.00</td>
<td>Sips</td>
<td>PSO</td>
<td>Endothermic</td>
<td></td>
</tr>
<tr>
<td>Luffa aegyptica peel</td>
<td>78.79</td>
<td>Langmuir</td>
<td>PSO</td>
<td>Endothermic</td>
<td></td>
</tr>
<tr>
<td>Chrysopogon zizanioide a roots</td>
<td>128.10</td>
<td>Freundlich</td>
<td>PSO</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

### ACKNOWLEDGEMENT

This research was supported by the University Grant (1001/PJKIMIA/8014061 and 304/PJKIMIA/6050434/1136) from Universiti Sains Malaysia.

### REFERENCES


