Two-Stage Batch Adsorber Optimisation for Malachite Green Removal Using Activated Waste Biomass

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Abstract

In this study, waste date stones biomass, from the seedless date products industry, have been treated and activated chemically using phosphoric acid to study its adsorption of malachite green dye, widely used in the plastics and textile industries. Phosphoric acid was used as an activating agent for the date stones and its adsorption capability has been measured and compared to the capacity of natural date stone powder. Experimental equilibrium data have been analyzed and correlated by three isotherm models: Langmuir, Freundlich, and SIPS (also called the Langmuir-Freundlich isotherm). The best fit for the experimental data for both treated and untreated date stone was the Langmuir-Freundlich isotherm. The surface areas and maximum malachite green adsorption capacities of the raw date stone and the acid treated date stone were 86.0 and 907 m²/g respectively; and maximum malachite green adsorption capacities were 31.5 and 64.7 mg/g respectively. A two-stage batch adsorber model has been developed to optimize the two-step adsorption process to remove malachite green and minimize the amount of adsorbent used for both untreated and treated date stones. The applications outputs include the minimum total adsorbent for designing various percentages dye removal, various effluent discharge concentrations and various initial dye concentrations.

1. INTRODUCTION

Waste biomass is now regarded as an effective raw material resource for the production of several products including fuel gas (Dinesh et al., 2018; Duman et al., 2018; Yang et al., 2016), fuel oil (Wang et al., 2018), syngas (Zacho et al., 2018) and biochars (Harsono et al., 2013; Mui et al., 2008; To et al., 2017; Valix et al., 2009). Several studies report the use of biomass wastes to produce activated carbons in a number of applications, for example, apricot (Gergova & Eser, 1996), bamboo (Ip et al., 2008), cherry stones (Lussier et al., 1994), coconut shell (Islam et al., 2017) olive stones (Alslaibi et al., 2013), peach stones (Molina-Sabio et al., 1995), pine cone (Saraghandi et al., 2015), plum stones (Parlayici & Pehlivan, 2017), sugar cane bagasse (McKay, 1998; Valix et al., 2004), rice husk and silk waste (McKay et al., 1987).

Activated carbons have been widely used for the treatment of many effluent types and malachite green is a widely used commercial dye in several industries but the dye has a damaging effect on plants and animals in the environment after ingestion or inhalation (McKay, 1995). However, the dye has generated much concern regarding its use due to its reported toxic effects (Srivastava et al., 2004). Many adverse effects from the consumption of the dye due to its carcinogenic, genotoxic, mutagenic and teratogenic properties in animal studies have been reported (Culp et al., 1999).

In the present study, date stones/pits have been used because of their very low ash content (below 3 wt%) as a precursor for producing activated carbons with a high carbon content (Habib & Ibrahim, 2009). The physical activation of date stones produced a much lower capacity carbon where the pore volume and surface areas were not reported (Banat et al., 2003). However, activated carbon based date pits have been shown to be effective in removing phenol from petroleum refinery wastewater (El-Naas et al., 2010). The removal efficiency of phenol by activated date pits is higher at 169 mg/g than activated carbons at weak acidic conditions (Merzougui et al., 2011) and significant for methylene blue, capacity 485 mg/g (Abbas & Ahmed, 2016). This “eco-friendly” adsorbent has to also proven applicable in removing heavy metals (Awwad et al., 2013).
2. EXPERIMENTAL SYSTEMS

In this study, we have compared the ability of natural raw date stone, NDS, and phosphoric acid activated date stone, PAADS, for the adsorption of malachite green dye. Adsorption tests were carried out to determine the malachite green dye equilibrium data for the adsorption process. The results were optimized by testing different equilibrium isotherms and different error analysis methods to determine the best fit isotherm and isotherm parameters.

2.1 Experimental Materials – Date Stones

Natural raw date stones, supplied by a local company, from their dateless seed products plant in Qatar. Only cleaning and washing were applied to remove dust and then two different types of date stone adsorbent were used to test their adsorption capacity on malachite green dye. The following section describes the treatments which were applied to the date stones. The modified date stones were then tested to assess their adsorption capacity using malachite green dye.

2.1.1 Natural date stone (NDS):

The first group of date stone was washed and dried without any physical or chemical activation. The washing took place by using distilled water to remove the soluble impurities and dust from the sample. The sample was treated chemically using nitric acid of a concentration of 0.1M for 1 hr. After that, the sample was soaked in methanol for the same time period to clean the sample from any organic and inorganic matter. Finally, the “cleaned” sample was dried for two days in an oven at 80 °C, crushed in a mechanical grinder, and sieved through the BSS-25 sieves to remove relatively large particles. The remaining material is referred to as natural date stone, NDS, and can be used as an adsorbent. This group will be referred to as “untreated date stone”. Equilibrium data show the amount of malachite green dye adsorbed after a sufficient time period to reach equilibrium.

2.1.2 Phosphoric acid activated date stone (PAADS)

The batch of NDS was treated with 30% concentration o-phosphoric acid, $H_3PO_4$, using an impregnation ratio of 2:1, as an activating agent. The resulted matter was heated in a muffle furnace in the same manner of the second group. To neutralize any remaining acid, the charred matter was cooled and washed with dilute ammonia solution. To ensure pH neutralization, the solution was washed with distilled water until the pH measured was exactly 7. Then, the solution was filtered and dried at 80 °C in an incubator overnight. Finally, the neutral dry sample was sieved through a 1.18 mm sieve after crushing. This batch of modified date stones will be referred to as “chemically treated date stone”, PAADS.

2.1.3 Properties of the date stones

The total pore volume, mean pore diameter, and BET surface area of the two different of date stone biomass products were measured. Table 1 shows the measured properties. The PAADS date stone had the highest total pore volume, mean pore diameter, and the largest surface area among the two types of date stones.

<table>
<thead>
<tr>
<th>Date stone</th>
<th>Total pore volume (cm$^3$/g)</th>
<th>Mean pore diameter (nm)</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDS</td>
<td>0.21</td>
<td>2.31</td>
<td>85.74</td>
</tr>
<tr>
<td>PAADS</td>
<td>0.55</td>
<td>2.48</td>
<td>908.6</td>
</tr>
</tbody>
</table>

2.2 Experimental Materials – Malachite Green Dye (MG)

Malachite green dye was used as the commercial dye supplied by B.D.H Chemical Ltd., Pool, England. Its chemical formula is $C_{23}H_{25}CIN_2$, maximum wavelength of absorbance is $\lambda_{\text{max}} = 617$ nm and molecular weight of 364.9 g/mol. The solution’s concentration was altered by diluting the dye as supplied with distilled water. Figure 1 shows the molecular structure of malachite green.
Malachite green has a wide range of industrial applications. The dye is used to color plastics, silk, leather, paper, and other materials. However, the dye has a damaging effect on plants and animals in the environment and also affects humans as it is considered toxic for the human respiratory system and can cause infertility (Culp & Beland, 1996; Gerundo et al., 1991). Malachite green is considered to be one of the most recalcitrant pollutants due to its resistance to light degradation and oxidizing agents (Srivastava et al., 2004).

### 2.3 Adsorption Experiments

All of the adsorption tests were carried out at 20 °C using a temperature-controlled shaker by mixing 3 g of adsorbent with malachite green solutions of specific concentrations in plastic bottles. The shaker agitation speed was set at 250 rpm. The initial and final concentrations of the sample solution were measured and recorded. The amount of adsorption was calculated using the mass balance equation shown below. The amount of adsorbed malachite green was assumed to be equal to the amount of the dye removed from the solution.

\[
\text{Amount of dye adsorbed} = \text{Amount of dye removed} \quad (1)
\]

\[
m (q_0 - q_e) = -V (C_0 - C_e) \quad (2)
\]

Rearranging the equation for \( q_e \):

\[
q_e = \frac{V}{m} (C_0 - C_e) \quad (3)
\]

where, \( q_e \) is the amount of dye adsorbed at equilibrium in mg/g, \( q_0 \) is the amount adsorbed at time zero, which is equal to 0, \( V \) is the volume of the solution in liters, \( m \) is the mass of the adsorbent in grams, \( C_0 \) is the initial concentration of the dye in mg/L, and \( C_e \) is the remaining dye concentration at equilibrium in mg/L. The time for the system to reach equilibrium was measured to be six hours. However, the isotherm studies were carried for 24 hours to ensure the equilibrium.

### 3. MODELING THEORY AND MODELS

#### 3.1 Isotherm Models

It is important to establish the correct, “best fit”, isotherm in order to establish the correct design capacity of a process treatment plant, the optimization of batch adsorbers and fixed bed adsorbers. The raw data provided were correlated using three of the most standard isotherm models and have been subjected to an error analysis using the SSE, sum of the square of the errors, method. The results are shown in Table 2. The models used are represented as follows.
3.1.1 Langmuir isotherm

The Langmuir adsorption model describes adsorption assuming that the adsorbate behaves like an ideal solute and follows Avogadro’s law (Langmuir, 1916). This model is popular in determining the activated carbon adsorption performance by quantifying the gas-solid and solid-liquid phase adsorption. The Langmuir isotherm is based on several assumptions: the adsorbed molecules do not interact among each other; adsorption occurs through the same mechanism and in a uniform manner along the adsorbent’s surface; and that adsorption occurs in a monolayer which means that molecules deposit only at the free surface of the adsorbent and cannot deposit on one another. Plotting \( q_e \) versus \( C_e \) for Langmuir shows a plateau which defines the point of equilibrium saturation where no further adsorption can take place due to lack of free space. The Langmuir isotherm is represented by Equation (4):

\[
q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)
\]

where \( q_m \) (mg/g) and \( b \) (L/mg) are Langmuir adsorption capacity constant and energy constant of adsorption, respectively.

3.1.2 Freundlich isotherm

The Freundlich adsorption model is similar to the Langmuir model with modification (Freundlich, 1906). It describes the non-ideal adsorption and indicates linear fit for log-log plot of adsorption data. The Freundlich isotherm is an empirical equation; it is based on observation rather than theory. It can be applied to multilayer adsorption with non-uniform distribution. Thus, the Freundlich isotherm is popular in heterogeneous systems, where the adsorption forces are different along the adsorbent’s surface, and the slope determines its heterogeneity level. The Freundlich isotherm is represented by Equation (5):

\[
q_e = k_F C_e^{1/n} \quad (5)
\]

where, \( k_F \) (mg/g)*(L/mg) and \( 1/n \) are indications of the adsorption capacity and surface heterogeneity, respectively. \( 1/n \) ranges between 0, more heterogeneous, and 1, more homogeneous.

3.1.2 Langmuir-Freundlich isotherm (SIPS)

The Langmuir-Freundlich isotherm (Sips, 1948) is a combined form of the Langmuir and Freundlich expressions to predict heterogeneous adsorption systems. At low concentrations of pollutants, the SIPS isotherm tends to be closer to the Freundlich heterogeneous isotherm whereas at high concentrations, it tends to become closer to the Langmuir monolayer isotherm. The Sips isotherm is represented by the following equation (6):

\[
q_e = \frac{K_{LF} C_e^{b_{LF}}}{1 + a_{LF} C_e^{b_{LF}}} \quad (6)
\]

where, \( K_{LF} \) (L/g) and \( a_{LF} \) are the Langmuir-Freundlich isotherm constants and \( b_{LF} \) is the isotherm exponent.

The error analysis results in Table 2 show that the Langmuir and the Langmuir-Freundlich isotherms describe the experimental equilibrium results very well with the Langmuir-Freundlich isotherm showing a better correlation. Consequently, the Langmuir–Freundlich equation has been selected for use in the optimization model in section 3.2.
Table 2. Isotherm models parameters for adsorption of MG by PAADS and RDS.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>PAADS</th>
<th>RDS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0.174</td>
<td>0.00583</td>
</tr>
<tr>
<td>q_m</td>
<td>64.7</td>
<td>29.5</td>
</tr>
<tr>
<td>SSE</td>
<td>52.4</td>
<td>3.53</td>
</tr>
<tr>
<td><strong>Freundlich Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_F</td>
<td>26.7</td>
<td>1.22</td>
</tr>
<tr>
<td>1/n</td>
<td>0.165</td>
<td>0.476</td>
</tr>
<tr>
<td>SSE</td>
<td>404</td>
<td>16.8</td>
</tr>
<tr>
<td><strong>Langmuir-Freundlich Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K_{LF}</td>
<td>14.8</td>
<td>0.203</td>
</tr>
<tr>
<td>a_{LF}</td>
<td>0.221</td>
<td>0.0016</td>
</tr>
<tr>
<td>b_{LF}</td>
<td>0.840</td>
<td>1.34</td>
</tr>
<tr>
<td>SSE</td>
<td>36.2</td>
<td>1.30</td>
</tr>
</tbody>
</table>

3.2 Two-Stage Batch Adsorber Optimisation Model Development Using the Langmuir-Freundlich Correlation

The schematic for the two-stage batch adsorption process is presented in Figure 2.

![Figure 2: Schematic figure of a two-stage system](image)

Using the Langmuir-Freundlich isotherm model equation, the material balance for the stage 1 adsorber becomes:

\[
\frac{S_{s1}}{L_s} = \frac{C_0 - C_1}{q_1 - q_o} \quad (7)
\]
\[
\frac{S_{s1}}{L_s} = \frac{(C_0 - C_1)(1 + a_{LF}C_1^{b_{LF}})}{K_{LF}C_1^{b_{LF}}} \quad (8)
\]

For the stage 2 adsorber unit, it becomes:

\[
\frac{S_{s2}}{L_s} = \frac{C_1 - C_2}{q_2 - q_0} \quad (9)
\]

\[
\frac{S_{s2}}{L_s} = \frac{(C_1 - C_2)(1 + a_{LF}C_2^{b_{LF}})}{K_{LF}C_2^{b_{LF}}} \quad (10)
\]

The total amount of adsorbent used is:

\[
\frac{S_1 + S_2}{L_s} = \frac{1}{K_{LF}} \left( \frac{(C_0 - C_1)(1 + a_{LF}C_1^{b_{LF}})}{C_1^{b_{LF}}} + \frac{(C_1 - C_2)(1 + a_{LF}C_2^{b_{LF}})}{C_2^{b_{LF}}} \right) \quad (11)
\]

\[
\frac{d(S_1 + S_2)/L_s}{dC_1} \quad \text{was set equal to zero in order to determine the minimum total adsorbent required. Thus, the equation (11) becomes:}
\]

\[
\frac{1}{K_{LF}} \left[ b_{LF} \frac{1}{C_1^{b_{LF}}} \left( \frac{C_0}{C_1} + 1 \right) + \frac{1}{C_1^{b_{LF}}} \right] = \frac{1}{K_{LF}C_2^{b_{LF}}} \quad (12)
\]

Let

\[
X = \left( \frac{C_1}{C_2} \right)^{b_{LF}} - b_{LF} \frac{C_0}{C_1} - 1 + b_{LF} \quad (13)
\]

The intermediate concentration, \( C_1 \), was determined by setting the value of \( X \) in Equation (13) to be zero using the solver add-in with Microsoft Excel spreadsheet. Thus, the amount of adsorbent of required for each stage could be determined by Equations (11) and (13).

4. RESULTS AND DISCUSSION

4.1 Equilibrium studies

Based on the SSE values the Langmuir-Freundlich or SIPS isotherm provides the best correlation of the experimental equilibrium results. The type of isotherm provides some information about the nature of the adsorption process. In both cases, RDS and PAADS, the Langmuir and Langmuir-Freundlich are the two best fit isotherms. The Langmuir only model is indicative of a monolayer adsorption, in which the isotherm will plateau when the maximum saturation capacity is reached, the adsorption process occurs only at one type of site and all these sites have equal energy. The Langmuir-Freundlich represents a variation on this theme with some heterogeneity but with adsorption at similar energy level sites. Both curves in Figure 3 show this tendency towards a plateau over the last 4 or 5 points.
4.2 Optimisation Studies

4.2.1 Untreated Raw Date Stones – RDS

The required amount of activated date stone by different treatments to reduce the final effluent concentration of MG to 0.5%, 1%, 5%, 10% and 20%, and to reduce the final effluent concentration of MG to fixed values of 0.5, 1, 2, 5, 10 mg/g were investigated. The parameters of Langmuir-Freundlich (Sips) model were used to model the untreated date stones. Figure 4 (a)-(e) are the summary of the optimised amount of untreated date stone carbon required when the final effluent concentration of MG is 0.5%, 1%, 5%, 10% and 20% of the initial concentration.
4.2.2 Phosphoric Activated Date Stones

The required amount of activated date stone to reduce the final effluent concentration of MG to 0.5%, 1%, 5%, 10% and 20%, and to reduce the final effluent concentration of MG to fixed values of 0.5, 1, 2, 5, 10 mg/g were investigated. The parameters of Langmuir-Freundlich (Sips) model were used to model the phosphoric acid chemically treated date stones. Figure 5 (a)-(e) are the summary of the optimised amount of chemically activated date stone carbon required when the final effluent concentration of MG is 0.5%, 1%, 5%, 10% and 20% of the initial concentration.
Fig. 5. Minimum total amount of chemically activated date stone carbon for removal of MG using Langmuir-Freundlich model for different removal rate (a), (b), (c) and different fixed values of final concentration of MG in effluent (d), (e), (f).

4.2.3 Comparison to a Single Stage Adsorber

The required amount of activated date stone to reduce the final effluent concentration of MG to 0.5% and 5% by a single stage adsorber has been investigated. The parameters of the Langmuir-Freundlich (Sips) model were used to model the phosphoric acid chemically treated date stones, PAADS. Table 3 compares the amount of PAADS carbon required in a single stage adsorber and two-stage adsorber when the final effluent concentration of MG is 0.5% and 5%.
### Table 3. Amount of PAADS adsorbent required for a single stage adsorption vs two-stage adsorption

<table>
<thead>
<tr>
<th>Removal %</th>
<th>99.50%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 ) (mg/L)</td>
<td>( S ) (g)</td>
<td>( S_1+S_2 ) (g)</td>
</tr>
<tr>
<td>50</td>
<td>11.5</td>
<td>2.5</td>
</tr>
<tr>
<td>100</td>
<td>13.5</td>
<td>3.5</td>
</tr>
<tr>
<td>150</td>
<td>15.1</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>16.4</td>
<td>5.0</td>
</tr>
<tr>
<td>250</td>
<td>17.7</td>
<td>5.9</td>
</tr>
<tr>
<td>300</td>
<td>18.8</td>
<td>6.4</td>
</tr>
<tr>
<td>350</td>
<td>19.9</td>
<td>7.5</td>
</tr>
<tr>
<td>400</td>
<td>21.0</td>
<td>8.3</td>
</tr>
<tr>
<td>450</td>
<td>22.0</td>
<td>9.2</td>
</tr>
<tr>
<td>500</td>
<td>23.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

5. CONCLUSION

Activated carbon has been prepared and tested using the waste date stones from the seedless date industry. Equilibrium studies were studied for the adsorption of malachite green from aqueous solution by untreated date stone and an activated carbon based on phosphoric acid treated date stone powder. The equilibrium data have been analyzed by the Langmuir, Freundlich and Langmuir-Freundlich equilibrium isotherm models and the characteristic parameters for each isotherm have been determined. The best fit isotherm for both adsorbents was the Langmuir-Freundlich model. Then, the best fit isotherm was used to minimize the amount of adsorbent required in a two-stage batch adsorber design and application operation. It indicates that the total amount of adsorbent increases either with increasing initial concentration of malachite green dye, higher removal rate, and with an increase in the dye solution volume. A comparison of the amount of adsorbent required between a single stage adsorption process and two-stage adsorption showed that the performance of the latter was significantly better. As a result, the two-stage system resulted in roughly 33% of the adsorbent as a one-stage system to remove the same amount of MG. For a commercial treatment process, the economic comparison between the adsorbent saving versus the increased cost of the two-stage adsorber over the single-stage adsorber needs to be investigated. Overall waste date stone activated carbon has considerable potential for commercial application.

References


