Adsorption of Malachite Green Dye onto Activated Carbon Derived from Durian Peel

SARAWUT SRIKHUN, SAMORN HIRUNPRADITKUN, KAMCHAI NUITHITIKUL*
Department of Chemical Engineering
King Mongkut’s University of Technology North Bangkok
1518 Piboonsongkram Road, Bangsue, Bangkok, 10800
THAILAND
Kamchai_Fius@yahoo.co.uk    http://www.che.kmutnb.ac.th

Abstract: The feasibility study of preparing activated carbon from durian peel by physical activation with carbon dioxide was investigated. Two pyrolysis conditions were employed and compared: nitrogen atmospheric and vacuum pyrolysis. After synthesis of activated carbon, influence of acid treatment (2 M HCl) on properties of the activated carbon was investigated. The results showed that activated carbon synthesized under vacuum pyrolysis exhibited better properties (BET surface area, pore volume) than that synthesized under nitrogen atmospheric pyrolysis. Treatment of activated carbon synthesized from both pyrolysis conditions with HCl solution increased BET surface area and pore volume. The pseudo-second-order kinetics model represented the adsorption of malachite green on HCl-treated activated carbons better than the pseudo-first-order kinetics model. The experimental adsorption equilibrium data were fitted to Langmuir and Freundlich models, with the former providing the best fit. The maximum adsorption capacities of activated carbons in this study were very high in comparison to those found in previous studies. Therefore durian peel is a promising raw material in the production of activated carbon for effective removal of malachite green, contributing to the conservation of the global environment.

Key-Words: Durian peel, Activated carbon, Malachite green, Adsorption, Isotherm, Kinetics

1 Introduction

Malachite green dye is commonly used for the dyeing process and in the manufacturing of paints and printing inks [1]. It is also used as a fungicide and antiseptic in aquaculture and fisheries [2]. Despite its industrial importance, malachite green poses several risks to the consumers, including its effects on the immune system and reproductive system as well as its genotoxic and carcinogenic potentials [2]. Therefore effective removal of malachite green from wastewater is necessary.

Activated carbon is reported to be a high effective adsorbent of various dyes [3]. However commercial activated carbon in some countries is expensive. Therefore the production of activated carbon from renewable and agricultural wastes is an area of interesting worldwide due to its economic and environmental benefits.

Durian (Durio zibethinus Linn.) is a widely known fruit in Southeast Asia. Direct disposal of durian peel will increase the amount of agricultural waste. Therefore it would be economically attractive if durian peel can be used as a raw material for the production of effective activated carbon.

To the best of our knowledge, there are very few studies in the production and application of activated carbon from durian peel. Durian peel-based activated carbon was reported by Chandra et al. [4, 5]. Chemical activation using KOH was applied to the production of durian peel-based activated carbon and the synthesized activated carbon was used for the adsorption study of methylene blue [4].

It is commonly known that activated carbon can be synthesized from physical activation, chemical activation or both together. Since chemicals used in the production with chemical activation are harmful, and most chemicals are more expensive and corrosive than oxidizing gases used in the production of activated carbon with physical activation [6], it is interesting to produce activated carbon from durian peel with physical activation. Therefore this study aimed to investigate the properties and adsorption capacity of activated carbon prepared from durian peel with physical activation using carbon dioxide (CO₂). Two-step process was employed: nitrogen atmospheric or vacuum pyrolysis, followed by CO₂ activation at different temperatures. Additionally influence of acid treatment after the synthesis of activated carbon was examined. Adsorption capacity, kinetics and isotherm of malachite green onto activated carbon derived from durian peel were finally carried out.
2 Experimental

2.1 Preparation of activated carbon

Durian peel was acquired locally and cut to smaller pieces (1x1 cm² in size). Drying of durian peel was then carried out in an oven at 80 °C for 24 h in order to reduce the moisture content. The dried durian peel was used for the preparation of activated carbon which took place in an electrical furnace (Model N7, Naber). 100 g of dried durian peel was carbonized either under nitrogen atmospheric or vacuum pyrolysis, and activated with CO₂.

In the carbonization process, the furnace temperature was raised from room temperature to a required activation temperature (700, 800 or 900°C) with the heating rate of 5 °C min⁻¹. During the heating, either nitrogen gas with the flow rate of 150 mL min⁻¹ or vacuum pressure (56 kPa) was applied. Once the desired activation temperature was reached, the activation process with CO₂ took place. 300 mL min⁻¹ of CO₂ was fed into the furnace for 1 h. The obtained activated carbon was cooled down to room temperature under nitrogen atmosphere. Activated carbons synthesized under nitrogen atmospheric and vacuum pyrolysis were assigned here as AN and AV respectively. For the study on the influence of acid treatment, both AN and AV were immersed in hydrochloric aqueous solution (2 M HCl) for 24 h. Both HCl-treated and untreated AN and AV were then washed with deionized water several times until the pH of washing water was neutral. Finally the activated carbons were dried at 110°C for 3 h. Prior to use, they were grounded to a desired mesh size of less than 0.18 mm and kept in a desiccator.

2.2 Characterization

Proximate analysis of durian peel was carried out using thermogravimetric analyzer (ASTM D 5142-90). Cellulose (α-cellulose) and hemicellulose (β-cellulose and γ-cellulose) were examined by TAPPI T 203 om-93 method, while lignin was examined by TAPPI T 222 om-88 method. Heating value was measured using Bomb calorimeter. Bulk density of activated carbons was evaluated according to JIS 1474-1975. Yields of activated carbons were calculated based on the weight of dried durian peels initially added into the furnace. BET surface area, pore volume and average pore diameter were obtained from nitrogen adsorption with Quantachrome Autosorb Automated Gas Sorption.

2.3 Adsorption study

In the study on adsorption kinetics of malachite green, a set of volumetric flasks containing 25 mL of malachite green solutions at pH = 5 was prepared. Different initial concentrations (337, 562, 784 and 1000 mg L⁻¹) of malachite green were used. HCl-treated AN or HCl-treated AV (0.05 g) was added into each flask. The flasks were placed in an isothermal shaker (150 rpm) in which the temperature was maintained at 30 ± 1 °C. The flasks were taken out from the shaker at various time intervals and solutions were taken for analysis. Similar procedure was carried out with another set of flasks containing the same dye concentrations but without activated carbon to be used as a blank. The amount of adsorbed malachite green per unit mass of activated carbon at any time t, q_t (mg g⁻¹), was calculated by:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  (1)

where \( C_0 \) and \( C_t \) (mg L⁻¹) are the liquid-phase concentrations of malachite green at initial and time t, respectively. \( V \) is the volume of solution (L), and \( m \) is the amount of activated carbon used (g).

For the study on adsorption isotherm of malachite green, a set of volumetric flasks containing 25 mL of malachite green solutions with initial concentration of 1000 mg L⁻¹ was prepared. A variation in amount (0.01 - 0.13 g) of HCl-treated AN or HCl-treated AV was added into each flask. The flasks were placed in an isothermal shaker (150 rpm) in which the temperature was maintained at 30 ± 1 °C. Samples were taken for analysis after 72 hours of adsorption to ensure the equilibrium was achieved. The amount of adsorbed malachite green per unit mass of activated carbon at equilibrium, \( q_e \) (mg g⁻¹), was calculated by:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  (2)

where \( C_e \) (mg L⁻¹) is the liquid-phase concentration of malachite green at equilibrium.

To determine dye concentrations, samples after adsorption were centrifuged at 2500 rpm. The clarified supernatant solutions were carefully decanted to be analyzed with a double beam UV/VIS spectrophotometer (UV500 model, UNICAM) using the wavelength of 617 nm. The concentrations of the solutions were calculated from a calibration curve.

3 Results and Discussion

3.1 Properties of durian peel

Properties of durian peel precursor are shown in Table 1. The proximate analysis found that durian peel had volatile matter of 69.82%, fixed carbon
21.42%, moisture 4.54% and ash 4.22%. The high fixed carbon and low ash contents are typically required properties of raw materials to be used for the production of activated carbon. A comparison in properties of durian peel with coconut shell [7], which is typically used as a raw material for the production of commercial activated carbon, showed that durian peel had similar amounts of volatile matter and fixed carbon to those of coconut shell, suggesting a potential of durian peel to be used as a raw material for the production of commercial activated carbon.

Table 1 Properties of durian peel

<table>
<thead>
<tr>
<th>Properties</th>
<th>Durian peel</th>
<th>Coconut shell [7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating value (cal g⁻¹)</td>
<td>3620.7</td>
<td>-</td>
</tr>
<tr>
<td>Proximate analysis (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture content</td>
<td>4.54</td>
<td>9.35</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>69.82</td>
<td>68.28</td>
</tr>
<tr>
<td>Ash</td>
<td>4.22</td>
<td>1.21</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>21.42</td>
<td>21.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>11.9</td>
</tr>
<tr>
<td>Cellulose</td>
<td>34.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>16.8</td>
</tr>
</tbody>
</table>

3.2 Properties of activated carbons

Properties of AN and AV synthesized at various temperatures (700, 800 or 900°C) are summarized in Table 2. At a specific temperature, the yield of activated carbon synthesized from nitrogen atmospheric pyrolysis was higher than that from vacuum pyrolysis. This indicates that the volatilization and carbon-CO₂ reaction take place on activated carbon synthesized from vacuum pyrolysis with a greater extent than that synthesized from nitrogen atmospheric pyrolysis. This is in agreement with Cao et al. [8]. The yields of both AN and AV were found to decrease with activation temperature. This is because more volatiles are released at higher temperatures, corresponding to the study of Lua & Yang [9].

The bulk density of activated carbon decreased with activation temperature because increasing activation temperature helps release more organic components, leaving the char’s internal and external surface less occupied by deposits. When this char is preceded to the activation process, the reaction between carbon and CO₂ is likely to occur more easily. As a result, more porous structure is developed and, in turn, bulk density is reduced.

As can be seen from Table 2, both BET surface area and pore volume of AN and AV increased when the activation temperature was increased. It is also important to note that the activated carbon synthesized under vacuum pyrolysis had higher BET surface area and pore volume than that synthesized under nitrogen atmospheric pyrolysis. This again indicates more volatilization and reaction occurring with the synthesis under vacuum pyrolysis.

Typically specific surface area is the key factor influencing the adsorption capacity of activated carbon. Adsorption capacity usually increases with specific surface area. To commercially produce effective activated carbon from durian peel, therefore, vacuum pyrolysis followed by CO₂ activation at very high temperature (e.g. 900°C) is recommended.

Chandra et al. [4] synthesized activated carbon from durian peel with chemical activation using KOH. The BET surface area and pore volume of their activated carbon were 991.82 m² g⁻¹ and 0.471 mL g⁻¹ respectively. Comparing those properties with ours, the activated carbon synthesized under vacuum pyrolysis, followed by CO₂ activation at temperature of 900°C had slightly lower BET surface area (951 m² g⁻¹) but higher pore volume (0.61 mL g⁻¹).

Owing to the highest BET surface area and pore volume of activated carbon pyrolyzed and activated at 900°C, further study in the effect of acid (2M HCl) treatment was carried out with AN and AV prepared from this temperature.

Table 2 Properties of activated carbon synthesized under nitrogen atmospheric (AN) or vacuum pyrolysis (AV) at various temperatures

<table>
<thead>
<tr>
<th>Properties</th>
<th>AN synthesized at</th>
<th>AV synthesized at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700 °C</td>
<td>800 °C</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>27.26</td>
<td>25.86</td>
</tr>
<tr>
<td>Bulk density (g mL⁻¹)</td>
<td>0.50</td>
<td>0.39</td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>119</td>
<td>294</td>
</tr>
<tr>
<td>Pore volume (mL g⁻¹)</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>3.42</td>
<td>2.76</td>
</tr>
</tbody>
</table>
3.3 Effect of acid treatment

Table 3 represents BET surface area and pore volume of AN and AV synthesized at 900°C and treated with HCl solution in comparison to untreated AN and AV.

Table 3 Effect of HCl treatment on surface area and pore volume of AN and AV synthesized at 900°C

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (mL g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AN</td>
<td>659</td>
<td>0.40</td>
</tr>
<tr>
<td>HCl-treated AN</td>
<td>748</td>
<td>0.46</td>
</tr>
<tr>
<td>Untreated AV</td>
<td>951</td>
<td>0.61</td>
</tr>
<tr>
<td>HCl-treated AV</td>
<td>1015</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Treatment of activated carbon with HCl solution significantly improved BET surface area and pore volume. For activated carbon synthesized under nitrogen atmospheric pyrolysis, BET surface area and pore volume increased from 659 m² g⁻¹ and 0.40 mL g⁻¹ to 748 m² g⁻¹ and 0.46 mL g⁻¹ respectively. For activated carbon synthesized under vacuum pyrolysis, BET surface area and pore volume increased from 951 m² g⁻¹ and 0.61 mL g⁻¹ to 1015 m² g⁻¹ and 0.66 mL g⁻¹ respectively. Such increase is due to the removal of inorganic matter by acid solution. Wang & Zhu [10] found that acid (HCl, HNO₃) treatment of activated carbon could slightly increase BET surface area due to the removal of some mineral matter. Ahmedna et al. [11] similarly stated that the treatment of activated carbon with HCl solution could remove surface ash particles.

It is noted that after the acid treatment, our activated carbon synthesized under vacuum pyrolysis had higher BET surface area and pore volume than that prepared from chemical activation [4]. Owing to the improved BET surface area and pore volume, HCl-treated AN and HCl-treated AV were used for the study on adsorption kinetics and isotherm of malachite green.

3.4 Adsorption kinetics of malachite green

To evaluate adsorption kinetics, two common models were used: pseudo-first-order and pseudo-second-order kinetic models as shown in equations (3) & (4) respectively:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)
\]

\[
t = \frac{1}{k_2q_e} + \frac{1}{q_e}t \quad (4)
\]

where \(k_1\) (min⁻¹) and \(k_2\) (g mg⁻¹ min⁻¹) are the rate constants of pseudo-first-order and pseudo-second-order adsorptions respectively.

Fig. 1 Adsorption kinetics: (a) Pseudo-first-order of HCl-treated AN; (b) Pseudo-first-order of HCl-treated AV; (c) Pseudo-second-order of HCl-treated AN; (d) Pseudo-second-order of HCl-treated AV
Comparison between experimental data with the two kinetics models for malachite green adsorption of HCl-treated AN and HCl-treated AV was made and plotted in Fig. 1. The pseudo-second-order kinetics model better represented the adsorption of malachite green on activated carbons both synthesized under nitrogen atmospheric and vacuum pyrolysis. This was confirmed by the correlation coefficients (R²); pseudo-second-order model gave very high values of R² of more than 0.99 for both HCl-treated AN and HCl-treated AV.

3.5 Adsorption isotherms of malachite green
Two well-known adsorption isotherms, Langmuir and Freundlich, were used and compared in this study using R² as criteria. Equations (5) & (6) represent Langmuir’s isotherm model and its linear form respectively:

\[
q_e = \frac{q_{max} b C_e}{1 + b C_e} \tag{5}
\]

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \left(\frac{1}{q_{max}}\right) C_e \tag{6}
\]

where \(q_{max}\) (mg g⁻¹) and \(b\) (L mg⁻¹) are Langmuir constants in relevant to maximum adsorption capacity (monolayer capacity) and energy of adsorption respectively.

The Freundlich isotherm and its logarithmic form are given by equations (7) & (8) respectively:

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

\[
\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{8}
\]

where \(K_F\) and \(n\) are Freundlich constants in relevant to adsorption capacity and how favorable the adsorption process (adsorption intensity) respectively.

Fig. 2 represents the fitted equilibrium adsorption data to Langmuir and Freundlich isotherms. Isotherm parameters and the correlation coefficients, R², were calculated from the plots based on equations (6) & (8). Their values are summarized in Table 4.

![Fig. 2 Adsorption isotherms of malachite green on HCl-treated AN and HCl-treated AV](image)

![Table 4 Langmuir and Freundlich isotherm constants for adsorption of malachite green](table)

Based on the high values of R² (more than 0.90), the experimental equilibrium data was fitted to Langmuir and Freundlich isotherms. However, the Langmuir isotherm gave a better fit than the Freundlich isotherm for both HCl-treated AN (R² = 0.988 vs. 0.954) and HCl-treated AV (R² = 0.995 vs. 0.927). This suggests that monolayer adsorption of malachite green takes place on the homogeneous surface of activated carbon prepared from durian peel with physical activation. Adsorption activation energy is identical when each dye molecule adsorbs onto the activated carbon surface. Similar result on the suitability of Langmuir isotherm was observed by the adsorption of methylene blue onto activated carbon prepared from durian peel with chemical activation [4].

It is important to note that activated carbon in our study had very large maximum monolayer adsorption capacities \(q_{max}\) of malachite green in comparison to activated carbons derived from other materials: 263.6 mg g⁻¹ for bamboo-based activated carbon [12]; 116.3 mg g⁻¹ for waste apricot-based activated carbon [13]; 170.3 mg g⁻¹ for bagasse fly ash [14]; 92.6 mg g⁻¹ for rice husk-based activated carbon [15].

4 Conclusion
Activated carbon synthesized under vacuum pyrolysis exhibited better BET surface area and pore volume than that synthesized under nitrogen atmospheric pyrolysis. Treatment of activated carbon with HCl solution improved both BET surface area and pore volume. In the adsorption study the pseudo-second-order kinetics model
represented the adsorption of malachite green better than the pseudo-first-order kinetics model. The experimental adsorption equilibrium data were fitted to Langmuir and Freundlich models, with the former providing the best fit. The maximum adsorption capacities of activated carbons synthesized under nitrogen atmospheric and vacuum pyrolysis were very high in comparison to those reported in previous studies. Therefore durian peel is a promising raw material in the production of activated carbon for effective removal of malachite green.

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