Adsorption of Methylene Blue on Cardboard-Based Activated Carbons Treated with Zinc Chloride and Potassium Hydroxide

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Summary  
Activated carbons were derived from cardboard by carbonization, ZnCl₂ activation and KOH activation. The ZnCl₂-activated carbon samples showed a higher removal of methylene blue from water. The ZnCl₂-activated carbon prepared at 600°C (CB-Z₁₆₀₀) showed a greater adsorption amount of 227 mg/g, that would be directly associated with its well-developed pore properties compared with the other carbon samples. Among several experimental factors examined, the surface area was found to be the most influential factor for methylene blue adsorption onto the prepared activated carbons. It was also revealed that the methylene blue adsorption data were fitted well with the pseudo-second-order kinetics model and Langmuir isotherm model.

Key words: activated carbon, cardboard, KOH activation, methylene blue adsorption, zinc chloride activation

Introduction  
Activated carbon is a porous material, and is recognized to be useful as adsorbent, catalyst and capacitor 1-3. Activated carbon is mainly used as adsorbent for the uptake of gases and organic compounds. Although carbonaceous materials such as wood, coconuts shell and coal are widely employed as activated carbon precursor, several studies in recent years also attempted to capitalize on the abundance of agricultural residues and industrial by-products in the preparation of activated carbon 4, 5. Generally, activated carbon can be produced through physical and chemical activation, in which chemical activation has proven to be effective in producing activated carbon with highly pore development 6, 7. Dehydrating agents, namely ZnCl₂ and KOH are commonly used in the chemical activation method.

In Malaysia, the amount of municipal solid waste is kept in increasing, and often it is mainly buried in landfill due to low waste recycling rate 8. Although there were 291 landfill sites in Malaysia, those sites were decreased to 179 as of 2007 9. Hence alternate method of landfill is needed for waste management. Cardboard is among the common municipal solid wastes that is mainly used for packing and packaging purposes. An average of 280 tons per day of the municipal solid waste was discharged at Bakri landfill, and 5 % of those wastes were attributed to cardboard 10. Recycling of cardboard instead of using it for disposal or landfill would cause less impact on the environment. Some studies suggested that spent cardboard could be efficiently used as acoustic absorber and methane adsorbent 11, 12. Nowicki et al. reported a method of obtaining corrugated cardboard-based adsorbents by pyrolysis and physical activation 13. Hence, cardboard-based activated carbon may as well be prepared through chemical activation, thus promoting the recycling of waste such as cardboard.

In this study, activated carbons were prepared from cardboard through carbonization, ZnCl₂ activation and KOH activation. The activated carbons were evaluated by N₂ adsorption-desorption isotherms, and then adsorption capacity was investigated by methylene blue adsorption test.
Methods

Sample preparation

The hard cardboard (CB) is a waste material, which is commonly and widely distributed for packaging. It was obtained from a local manufacturer and to be used as activated carbon precursor. First, the CB was cut into pieces (3 × 10 × 45 mm) and oven-dried at 105°C overnight. Then, it was heated inside an aluminum foil-wrapped evaporating dish in a furnace at 500 and 600°C for 1 h. After cooling to room temperature, the sample was ground using pestle and mortar. Each sample was labelled as CB-T, where T is the heating temperature (°C). In carbonization at 700°C, aluminum foil was broken and the sample was ashed. Thus, cardboard was not treated at higher temperature than 600°C in this study.

The dried CB was mixed with zinc chloride solution at the ZnCl₂/CB weight ratio of 1 g/g, stirred for 6 h, and then the mixture was oven-dried at 105°C overnight. The mixture was heated inside an aluminum foil-wrapped evaporating dish in a furnace at 500 and 600°C for 1 h. Next, the sample was ground and washed with HCl and hot distilled water in a Soxhlet extractor, and then oven-dried at 105°C overnight. Each sample was labelled as CB-Z_T.

The dried CB was mixed with potassium hydroxide solution at the KOH/CB weight ratio of 1 g/g, stirred for 3 h, and then mixture was oven-dried at 105°C overnight. The remaining procedures were the same as earlier described for zinc chloride activation. The samples were designated as CB-K_Ts.

Characterization

The porous properties of carbon samples were measured through adsorption-desorption isotherms of nitrogen gas at −196°C with a specific surface area and pore size distribution analyzer (ASAP 2020, Micromeritics, USA). All samples were degassed at 300°C for 1 h prior to analysis. The specific surface area (S BET) was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume (V tot) was estimated by the quantity of gas adsorbed at a P/Po of 0.98. The micropore volume (V micr) was obtained using the t plot method. The mesopore volume (V meso) was calculated by the difference between V tot and V micr.

Methylene blue adsorption

Adsorption kinetics

Adsorption kinetics experiment for methylene blue in aqueous solution was performed in a batch system. The test solution was prepared by dissolving methylene blue powder in distilled water to a concentration of 100 mg/L or 500 mg/L. A 100 mg of the dried sample was added to 50 mL of methylene blue solution (100 mg/L for CB-T and 500 mg/L for other samples) and stirred at 110 rpm at room temperature for 4 h. The concentrations of methylene blue solution before and after the adsorption were measured using a UV-Vis spectrophotometer at 570 nm. The methylene blue adsorption at equilibrium (Qe) was calculated as,

\[ Q_e = \frac{(C_0 - C_e)V}{W} \]  

where \( C_0 \) (mg/L) is the initial concentration, \( C_e \) (mg/L) is the concentration at time \( t \), \( V \) (L) is the volume of solution, and \( W \) (g) is the mass of the sample. The experimental data were fitted to the pseudo-first-order and pseudo-second-order kinetics models.

The pseudo-first-order model is expressed as,

\[ \frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \]  

where \( Q_t \) (mg/g) is the amount of methylene blue adsorbed at equilibrium, and \( k_1 \) (h⁻¹) is the pseudo-first-order rate constant. Eq. (2) was integrated with the boundary conditions of \( t=0 \rightarrow t \), and \( Q=0 \rightarrow Q_e \). The integrated form of Eq. (2) is described as follows.

\[ \ln(Q_e - Q_t) = \ln(Q_e) - k_1t \]  

The values of \( k_1 \) and \( Q_e \) were calculated from the slope and intercept of the linear plot of \( \ln(Q_e - Q_t) \) versus \( t \).

The pseudo-second-order model can be represented by

\[ \frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \]  

where \( k_2 \) is the rate constant of the pseudo-second-order sorption kinetics [g/(mg h)]. Eq. (4) was integrated with the boundary conditions of \( t=0 \rightarrow t \), and \( Q=0 \rightarrow Q_e \). The integrated form of Eq. (4) is described as follows.

\[ \frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2Q_e^2} \]  

The values of \( k_2 \) and \( Q_e \) were estimated from the slope and intercept of the linear plot of \( t/Q_t \) against \( t \).

Equilibrium adsorption

The equilibrium adsorption experiment was performed in a batch system. A 100 mg of the dried sample was added to 50 mL of the methylene blue solution of various concentrations (5–100 mg/L for CB-T and 50–1000 mg/L for other samples) and stirred at 110 rpm at room temperature for 4 h. The concentrations of methylene blue solution before and after the adsorption were measured using a UV-Vis spectrophotometer at 570 nm. The methylene blue adsorption at equilibrium (Qe) was calculated as,

\[ Q_e = \frac{(C_0 - C_e)V}{W} \]  

where \( C_e \) (mg/L) is the concentration of methylene blue at equilibrium. The equilibrium data were fitted to Langmuir and Freundlich isotherm models. The Langmuir isotherm is represented by

\[ \frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}K_L} + \frac{1}{Q_{\text{max}}} \]  

where \( Q_{\text{max}} \) (mg/g) is the maximum adsorption capacity and \( K_L \) (L/mg) is the adsorption affinity. The Freundlich isotherm is given as,

\[ \ln(Q_e) = \ln K_F + \frac{1}{n}\ln(C_e) \]  

where \( K_F \) [(mg/g)/(L/mg)]⁻¹ and \( n \) are the Freundlich constants related to the adsorption capacity and intensity, respectively.

Results and Discussion

Sample properties

Table 1 gives the textural properties and yield of the prepared samples. The yield was calculated by,

\[ \text{Yield} = \frac{\text{Sample amount after activation (g)}}{\text{Sample amount before activation (g)}} \times 100 \]

The positive effect of each activation method was observed and
the porous properties of activated samples are higher than that of carbonized samples. The ZnCl₂ activation was clearly more effective than KOH activation in producing cardboard-based activated carbon with higher specific surface area. The influence of ZnCl₂ activation temperature is strong toward the pore development, as portrayed in Table 1 whereby CB-Z_600 possesses higher porous properties and more than twice the value of specific surface area than CB-Z_500. In ZnCl₂ activation mechanism, the swelling of ZnCl₂ creates the porosity without consuming the sample. Accordingly, the ZnCl₂ activated samples showed almost the same yield values with the carbonized samples²⁰. On the other hand, in KOH activation, the potassium compounds react with the carbon, therefore decreasing the yield of KOH activated samples²⁰.

**Adsorption kinetics**

The effect of contact time on the adsorption of methylene blue is shown in Fig. 1. The adsorption of carbonized samples and KOH activated samples reached equilibrium within 24 h, while the adsorption of ZnCl₂ activated samples took 48 h for equilibrium, although ZnCl₂ activated samples showed higher adsorption amount than the other samples. The adsorption kinetics parameters obtained by fitting the experimental data to the pseudo kinetics models are shown in Table 2. The pseudo-second-order model is better to describe the rate of adsorption of the prepared samples than the pseudo-first-order model. Accordingly to $k_2$, zinc chloride activated-carbons shows slower adsorption kinetics.

The relationships between the textural properties and methylene blue adsorption amount of the prepared samples are presented in Fig. 2. $S_{BET}$, $V_{total}$ and $V_{meso}$ exhibit positive correlation, indicating that these parameters are effective factor on methylene blue removal. Spagnoli et al. reported that pore volume (1.6-2.0 nm of pore size) and surface area showed good correlations with methylene blue adsorption amount⁷. Therefore, surface area and pore volume are contribut-

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| Sample  | $S_{BET}$ [m²/g] | $V_{total}$ [cm³/g] | $V_{micro}$ [cm³/g] | $V_{meso}$ [cm³/g] | Yield [%] |
|---------|-----------------|-------------------|-------------------|-------------------|----------|
| CB-600  | 14              | 0.05              | 0.00              | 0.03              | 39.9     |
| CB-500  | 2               | 0.03              | 0.00              | 0.01              | 42.6     |
| CB-Z_600 | 796             | 0.70              | 0.13              | 0.23              | 38.2     |
| CB-Z_500 | 309             | 0.19              | 0.05              | 0.04              | 35.3     |
| CB-K_600 | 154             | 0.27              | 0.01              | 0.13              | 13.7     |
| CB-K_550 | 156             | 0.23              | 0.02              | 0.09              | 14.5     |

**Table 1** Textural properties of activated samples

![Fig. 1 Adsorption amount of methylene blue onto each adsorbent as a function of time](image1)

**Table 2** Pseudo-first order and pseudo-second order kinetics parameters for methylene blue adsorption onto each adsorbent

| Sample  | $Q_e$ [mg/g] | $k_1$ [mg/g·h] | $R^2$ | $Q_e$ [mg/g] | $k_2$ [mg/g·h] | $R^2$ |
|---------|--------------|----------------|-------|--------------|----------------|-------|
| CB-600  | 15           | 9              | 0.203 | 0.753        | 15             | 0.0604 | 0.994 |
| CB-500  | 15           | 10             | 0.167 | 0.751        | 15             | 0.0546 | 0.991 |
| CB-Z_600 | 247          | 206            | 0.155 | 0.938        | 256            | 0.0013 | 0.999 |
| CB-Z_500 | 174          | 162            | 0.116 | 0.973        | 196            | 0.0007 | 0.987 |
| CB-K_600 | 107          | 57             | 0.304 | 0.833        | 116            | 0.0084 | 0.995 |
| CB-K_550 | 73           | 41             | 0.353 | 0.824        | 73             | 0.0427 | 0.995 |

**Fig. 2** The relationships between textural properties and methylene blue adsorption amount of prepared samples
ing factors to the amount of methylene blue adsorption. According to the correlation coefficient ($R^2$), $S_{BET}$ shows a good correlation towards methylene blue adsorption than $V_{total}$ and $V_{meso}$, implying that it is a strong influential factor on methylene blue adsorption onto the prepared cardboard activated carbons.

**Equilibrium adsorption**

The equilibrium data were analyzed using the Langmuir and Freundlich models. The model lines of Langmuir isotherms to the experimental data of the prepared samples are given in Fig. 3. The isotherm parameters are listed in Table 3. According to the correlation coefficient ($R^2$), the adsorption data were fitted well to the Langmuir model rather than the Freundlich model, revealing that the adsorption of methylene blue is monolayer and could occur on the homogeneous surface of cardboard-based carbon samples. CB-Z_600 and CB-K_600 show higher value of $K_L$ than CB-Z_500 and CB-K_550, respectively, pointing out that activated samples at higher temperature have more adsorption sites.

The adsorption capacity of methylene blue onto CB-Z_600 is compared with other adsorbents reported in the literature and shown in Table 4. It can be said that CB-Z_600 has the adsorption ability comparable to other adsorbents. To be used as a precursor of activated carbon, cardboard can be selected as one of the candidates.

**Conclusions**

Activated carbon was prepared from cardboard by ZnCl$_2$ activation and KOH activation. ZnCl$_2$-activated carbons showed the higher porous property than KOH-activated samples, indicating that ZnCl$_2$ activation is more effective activation method for cardboard than KOH activation. In ZnCl$_2$ activation, a higher activation temperature caused the enrichment of pore structure. The cardboard-based activated carbon with ZnCl$_2$ had a high adsorption capacity of methylene blue (227 mg/g) and the adsorption data were fitted well to the pseudo-second-order kinetic model and Langmuir model. These results suggested that zinc chloride activated cardboard-based carbon could be a superior adsorbent for uptake of dyes such as methylene blue.

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