Isotherm studies of methylene blue adsorption onto waste tyre pyrolysis powder-based activated carbons

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Abstract

This study was aimed to investigate the adsorptive ability of activated carbons derived from waste tyre pyrolysis powder by CO2 activation and ZnCl2 activation. The derived activated carbons and char were characterized for yield and specific surface area. Methylene Blue dye was used as a model pollutant to probe the performance of activated carbons. Result shows that the CO2-activated waste tyre pyrolysis powder exhibits a higher surface area of 97.0 m2/g, hence a greater methylene blue removal capacity of 47.2 mg/g. The methylene blue adsorption data by activated carbons and char obeyed the Langmuir isotherm with R2 of more than 0.99, describing the monolayer adsorption onto homogeneous surface. Physical activation of waste tyre pyrolysis powder using CO2 yields activated carbon with a promising performance for dyes removal from water.

Keywords: Activated carbon; adsorption; isotherm; methylene blue; waste tyre pyrolysiss powder

INTRODUCTION

Several industries such as paper, printing, dyestuff, textile, carpet, plastic, food and cosmetic used dyes to impart color to the products (Bensalah et al., 2009; Wrobel et al., 2001; Dawood et al., 2014). Every year, over 100,000 of commercially available dyes with more than 7 x 1012 ton of dyes are manufactured globally (Lee et al., 2006). Unfortunately, these dyes are eventually end up as industrial wastes, and consequently are discharged to the water bodies in the form of coloured wastewaters (Lee et al., 1999; Yagub et al., 2014).

According to Rangabashiyam et al. (2013) a number of treatment strategies including that of physical, chemical and biological methods have been applied to wastewater containing dye contaminants. Out of these, adsorption is a preferred technique because of several advantages, i.e., high efficiency, inexpensive, simplicity of design, ease of operation, ability to remove different colouring materials, works on ambient temperature and pressure, availability of various adsorbents, and small production of by-products and residues, thus an environmentally friendly process (Crimi, 2006; Ismail et al., 2013; Reza & Ahmaruzzaman, 2015). Activated carbon is a commonly used adsorbent for dye adsorption (Jha & Subedi, 2011; Ahmad et al., 2012). It is also suitable to remove various pollutants in air and water. Now, the search for eco-friendly and low cost precursor of activated carbon has been intensified on wastes and residues from industrial sectors.

Nearly 1.5 billion scrap tyres make their way into the environmental cycle every year (Rowhani & Rainey, 2016). One scrap tyre is produced per person per year, and this massive disposal of scrap tyres is common in many big cities (Turer, 2012). Two common strategies can be applied to scrap tyres, i.e., disposal and recycle. Through conventional disposal routes, the waste tyres are incinerated at high temperature or buried in a landfill. However, the disposal routes often result in a number of environmental pollutions and public health effects. The dumping areas, for example would become the breeding sites for flies and mosquitoes, while air pollution from the combustion of tyre increased the potential risk of cancer (Downard et al., 2015; Singh et al., 2015). Hence, the recycle of waste tyre is a long-term solution of this problem.

The end-of life tyre that can no longer be used normally undergone material or energy recovery (Toretta et al., 2015) The scrap tyre is ground into small pieces, and can be used as part of the construction material due to its physical characteristics, i.e., low weight, high drainage capacity, relatively compressible and low thermal conductivity. In energy recovery, low grade fuel can be obtained from waste tyre via pyrolysis. The recycle and recovery processes offer a lot of advantages such as economic return, minimization of hazardous emission and energy integration within the refinery (Hita et al., 2016). However, the pyrolysis of waste tyre inevitably produces secondary waste which is the solid residue, namely scrap tyre pyrolysis powder. Instead of sending the solid residue to a landfill for disposal, it is envisaged that the solid residue can be a promising precursor of activated carbon, which later can be used to treat various pollutants such as dyes and heavy metals. Previous studies reported the chemical activation of waste tyre pyrolysis powder for dyes removal from water (Zaini et al., 2014a,b; Lopez et al., 2013). However, the residue is already rich in carbon content, hence the pre-carbonization may not be necessary. Therefore, the present work was aimed at evaluating the effectiveness of physical activation of waste tyre pyrolysis powder using CO2, ZnCl2-activated sample and char were also employed for comparison purpose.
Methylene blue dye was used as model pollutant to probe the adsorption performance, and the adsorption data were analyzed using isotherm models.

**EXPERIMENTAL**

**Materials**

The waste tyre pyrolysis powder (WTP) of micro-sized particles was obtained from Bukit Batu Brickmill, Kulai, Johor. The is a side product of the low-grade fuel production by pyrolysis of scrap tyre material, and was used as a precursor in the preparation of activated carbons and char. All chemicals are of analytical reagents grade, and were supplied by QReC (Malaysia). CO₂ gas was supplied by Mega Mount Gases.

Methylene blue (MB), a cationic dye with empirical formula of C₂₅H₂₈N₂S₂Cl, molecular weight of 319.9 g/mol and colour index (CI) of 52015 was used as model pollutant in batch adsorption studies. Fig. 1 shows the chemical structure of methylene blue (Miculescu & Wiklund, 2010). It is a dark green powder that impart a blue solution when dissolved in water.

![Methylene blue molecule structure](image)

**Preparation and characterization of activated carbons**

Physical activation using CO₂ was carried out with assumption that the pre-carbonization is not necessary because the tyre pyrolysis powder is already rich in carbon content. The desired mass of WTP on a ceramic boat was placed at the centre of tubular furnace. CO₂ was allowed to flow inside the tubular furnace for 10 minutes to purge out air (oxygen) to prevent combustion during activation. Then, WTP was heated at 900°C in the presence of CO₂ for 5 h. The resultant sample was designated as AC-CO₂.

Chemical activation using ZnCl₂ was carried out with solid mass ratio of 1:1. The mixture of ZnCl₂ solution and WTP was stirred at 80°C for 2 h, and then it was oven-dried overnight at 110°C. After that, the impregnated sample was activated in a muffle furnace at 550°C for 2 h. Char was prepared by heating the precursor in air at 550°C for 2 h. The resultant samples were designated as AC-ZnCl₂ and AC-Char, respectively.

The WTP was characterized for oil content and ash content. The oil content was determined by dividing the weight of oil with the weight of residual WTP after extraction. The oil was extracted from the surface of WTP by refluxing hexane using Soxhlet. The recovery of oil and solvent was done using a rotary evaporator. The WTP was heated in a furnace at 850°C for 2 h. The ash content was calculated by dividing the mass of residue (left-over) with the initial weight of WTP.

Activated carbons and char were characterized for yield and specific surface area. The yield was calculated by dividing the final weight of resultant product with the initial weight of WTP. The specific surface area of activated carbons and char were obtained using a Pulse Chemisorb 2705 analyzer (Micrometrics, USA). A single-point Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area.

**Batch adsorption studies**

A series of methylene blue (MB) solution of varying concentrations were prepared through dilution from the stock solution. The concentrations are 5, 10, 20, 50, 70, 100, 120 and 150 mg/L. Thirty milligrams of sample was added into a flask containing 30 mL of MB solution of known concentration. The pH of the MB solution was unaltered. The mixture was allowed to equilibrate for 72 h at room temperature. The concentration of MB was analyzed using visible spectrophotometer (Halo Vis-10, Dynamica) at a wavelength of 664 nm (R² = 0.981).

The adsorption capacity, Qₑ (mg/g) was calculated using the following equations

\[
Qₑ = \frac{V(Cₒ - Cₑ)}{M}
\]

where V (L) is the volume of solution, M (g) is the mass of activated carbon, Cₒ (mg/L) is the initial concentration, Cₑ (mg/L) is the equilibrium concentration.

The adsorption data were analyzed using two well-known empirical isotherm equations, namely Langmuir and Freundlich models. Equations (2) and (3) represent the Langmuir isotherm model and its linear form, respectively,

\[
Qₑ = \frac{QₘₐₓKₐCₑ}{1 + KₐCₑ}
\]

\[
\frac{Qₑ}{Cₑ} = \frac{1}{Qₘₐₓ} + \frac{1}{QₘₐₓKₐ}
\]

where \(Qₘₐₓ\) (mg/g) is the maximum adsorption capacity and \(Kₐ\) (L/mg) is the Langmuir constant related to the affinity of the binding sites and energy of adsorption. The Langmuir isotherm is based on the assumption that the adsorption is a monolayer coverage on the homogeneous surface of adsorbent (Langmuir, 1918).

Freundlich model and its linear form are expressed in Equations (4) and (5), respectively,

\[
Qₑ = KₖCₑ^{1/n}
\]

\[
\ln Qₑ = \ln Kₖ + \frac{1}{n} \ln Cₑ
\]

where \(Kₖ\) (mg/g)(L/mg)^n is the Freundlich constant related to adsorption capacity and \(n\) is the empirical parameter related to adsorption intensity. The Freundlich isotherm describes a multilayer-type of adsorption onto the heterogeneous surface structure (Kundu & Gupta 2006). The isotherm parameters were determined from the slope and intercept of the best fit line with the equilibrium data.

**RESULTS AND DISCUSSION**

**Characteristics of activated carbons**

The oil content of WTP is 5.02%, while the ash content is 22.4%. The yields of CO₂-activated WTP, ZnCl₂-activated WTP and char are 48.2%, 73.3% and 91.9%, respectively. The lowest yield was recorded for AC-ZnCl₂. This could be resulted from the excessive burning-off at high temperature of activation (900°C). Likewise, the yield of AC-ZnCl₂ is lower than that of AC-Char because the former undergone impregnation with dehydrating agent (ZnCl₂), that may as well increase the liberation of volatiles at the expense of the pore development. However, it is also suggested that the impregnation procedure could result in the blockade of pores, and consequently yields activated carbon with low surface area. The properties of activated carbons and char are summarized in Table 1.

<table>
<thead>
<tr>
<th>Agent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
<th>pH</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>900</td>
<td>48.2</td>
<td>6.5</td>
<td>97.0</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>550</td>
<td>73.3</td>
<td>5.9</td>
<td>10.3</td>
</tr>
<tr>
<td>Air</td>
<td>550</td>
<td>91.9</td>
<td>6.3</td>
<td>58.0</td>
</tr>
</tbody>
</table>

**Effect of initial dye concentration**

Fig. 2 shows the equilibrium removal of methylene blue (MB) onto WTP-derived activated carbons and char. In general, the adsorption capacity rapidly increased when the concentration of MB...
increases. It signifies the affinity of MB towards the adsorption onto activated carbons and char is high. Increasing the concentration increases the driving force of mass transfer from the bulk solution to the adsorbent surface sites, and so increasing the amount of MB adsorption. At certain point of higher concentration, the capacity gradually slowed down, and the uptake seems to leveled-off. This stage is known as surface saturation or maximum capacity (Chen et al., 2011). From Fig. 2, the maximum capacities of MB were recorded as 17.5 mg/g, 32.9 mg/g and 45.1 mg/g for AC-ZnCl₂, AC-Char and AC-CO₂, respectively. This is directly proportional to the ascending order of the specific surface area of adsorbents produced in this work. The higher the surface area, the more the interaction probabilities between the surface sites and the MB molecules, hence the greater the removal capacity.

Equilibrium isotherm studies

Isotherm study indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when an equilibrium state is achieved in an adsorption process (Guo et al., 2013). Two isotherm models, namely Langmuir and Freundlich equations were used to describe the adsorption data. Fig. 3 shows the Langmuir plots of MB adsorption onto WTP-activated carbons and char. From the linear line of $C_e/Q_e$ against $C_e$, the Langmuir parameters can be determined from the gradient ($1/Q_{\text{max}}$) and intercept ($1/K_L Q_{\text{max}}$). The calculated values of $Q_{\text{max}}$ and $K_L$ are summarized in Table 2. The applicability of isotherm equation in explaining the adsorption mechanism is based on the coefficient of determination, $R^2$.

The separation factor, $R_L$ of Langmuir isotherm (dimensionless constant, $R_L = K_L C_o^{-1/}Q_{\text{max}}$) was used to validate the favourability of the adsorption process. Fig. 4 shows the $R_L$ profiles of activated carbons and char. The $R_L$ values for MB adsorption are between 0.0025 and 0.520, i.e., in the range of $0 < R_L < 1$. This shows that the adsorption of MB onto waste tyre pyrolysis powder based activated carbons and char is a favourable process.

Fig. 5 shows the Freundlich isotherm plots. The Freundlich parameters are summarized in Table 2. The Freundlich constant, $n$ represents the heterogeneous factor which suggests that the adsorption system is either linear when $n = 1$, chemical-type ($n < 1$) or physical-type ($n > 1$). The $n$ values ranging between 2.55 to 5.18 indicates that the process or adsorption system is of physical-type. In addition, the surface heterogeneity can be defined by $1/n$. The surface is said to be heterogeneous when $1/n$ approaches zero. In this work, the $1/n$ values are between 0.193 and 0.392, suggesting that the surface of adsorbents is highly heterogeneous.

From Table 2, the Langmuir isotherm exhibits higher $R^2$ than the Freundlich isotherm. Thus, the adsorption data of MB onto WTP-derived adsorbents obeyed the Langmuir isotherm to linear approximation. The Langmuir model assumes that the adsorption takes place at specific homogeneous sites within the adsorbent, at which once an adsorbate molecule occupies a site, no further adsorption can take place at that site. The acceptable fitting of Langmuir is supported by the close agreement between $Q_{\text{exp}}$ and $Q_{\text{max}}$. AC-CO₂ possesses the highest computed monolayer adsorption capacity of 47.5 mg/g.
Table 2 Parameters of isotherm models

<table>
<thead>
<tr>
<th></th>
<th>AC-\text{CO}_2</th>
<th>AC-\text{ZnCl}_2</th>
<th>AC-\text{Char}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>47.5</td>
<td>17.5</td>
<td>34.8</td>
</tr>
<tr>
<td>Langmuir Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>45.9</td>
<td>17.8</td>
<td>34.5</td>
</tr>
<tr>
<td>$K_L$</td>
<td>0.163</td>
<td>0.0371</td>
<td>2.06</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.997</td>
<td>0.995</td>
<td>0.991</td>
</tr>
<tr>
<td>Freundlich model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (mg/g)(L/mg)$^{1/n}$</td>
<td>1.00</td>
<td>7.51</td>
<td>7.94</td>
</tr>
<tr>
<td>$n$</td>
<td>2.55</td>
<td>5.18</td>
<td>2.90</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.845</td>
<td>0.928</td>
<td>0.938</td>
</tr>
</tbody>
</table>

Table 3 summarizes various waste tyre-based activated carbons for water pollutants removal. In general, it shows that the scrap tyre is a promising candidate to produce activated carbons with high specific surface area ranging from 50 m$^2$/g to 720 m$^2$/g under different activation strategies. Lopez et al. reported that the demineralization of raw material may be needed to reduce unnecessary minerals before activation. The shapes and physical appearances of waste tyre may not necessarily affect the development of surface area. However, previous works on waste tyre pyrolysis residue revealed a poor development of surface area upon chemical activation (Zaini et al., 2014a,b). This could be attributed to the activation strategies and the selection of activating agents. Chemical activation using ZnCl$_2$ and CaCl$_2$ may not be effective for waste tyre powder because of the nature of very fine powder particles, and that the material is already rich in carbon content (Zaini et al., 2014a). It should be noted that the material used in previous works has undergone pyrolysis at elevated temperature to produce low grade fuel, hence the carbonization step to increase the carbon content can be skipped, as demonstrated in this work (Zaini et al., 2014a,b). Definitely, physical activation displays a lower yield (ca. 59%) of activated carbon compared to chemical activation. However, the BET surface area of the resultant activated carbons by physical activation can be exceptionally high, which is up to 720 m$^2$/g, while that of chemical activation is around 200 m$^2$/g (Table 3). This shows that the pretreatment (impregnation) prior to activation does affect the development of surface area. Therefore, by using appropriate operating conditions, it is envisioned that an improved performance of activated carbons could be materialized by physical activation of waste tyre pyrolysis powder for water pollutants removal.

CONCLUSION

Waste tyre pyrolysis powder was used to synthesize activate carbons by CO$_2$ activation and ZnCl$_2$ activation, and char. The values of specific surface area are 97.0 m$^2$/g, 10.3 m$^2$/g and 58 m$^2$/g, respectively. The adsorption capacity increased with increasing methylene blue (MB) concentration, to a saturation point of maximum uptake. The MB adsorption is surface area-sensitive, and the increasing pattern of maximum capacity is in agreement with the ascending order of the surface area of adsorbents. The isotherm studies display a best fit of Langmuir model with the adsorption data, suggesting a monolayer-type of adsorption onto homogeneous surface sites. Inappropriate activation strategies may impede the development of surface area of waste tyre pyrolysis powder, thus jeopardizing the removal performance. Chemical activation, in particular may not be effective to activate this material. Nevertheless, this limitation could be overcome by appropriate physical activation.

Table 3 Preparation of waste tyre-based activated carbons for water pollutants removal.

<table>
<thead>
<tr>
<th>Physical appearance/shape</th>
<th>Treatment strategies</th>
<th>BET surface area (m$^2$/g)</th>
<th>Yield (%)</th>
<th>Carbon and (ash) content (%)</th>
<th>Target pollutant (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine powder</td>
<td>Remove surface oil: Activation: ZnCl$_2$, 1:1, 550°C, 1.5 h</td>
<td>288</td>
<td>91.2</td>
<td>(9.1) Methylene blue (154)</td>
<td>Zaini et al. (2014b)</td>
<td></td>
</tr>
<tr>
<td>Fine powder</td>
<td>Furnace, 250°C, 1.5 h</td>
<td>113</td>
<td>76.0</td>
<td>(9.1) Methylene blue (83)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fine powder</td>
<td>Remove surface oil: Activation: ZnCl$_2$, 1:1, 550°C, 1.5 h</td>
<td>95.9</td>
<td>72.3</td>
<td>- Reactive orange (81.3)</td>
<td>Zaini et al. (2014a)</td>
<td></td>
</tr>
<tr>
<td>Fine powder</td>
<td>Furnace, 250°C, 1.5 h</td>
<td>111</td>
<td>82.3</td>
<td>- Reactive orange (68.5)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Granulated form</td>
<td>Carbonization; CO$_2$, 850-950°C, 2-6 h</td>
<td>267</td>
<td>59.2</td>
<td>-</td>
<td>-</td>
<td>Feng et al. (2012)</td>
</tr>
<tr>
<td>Granulated form</td>
<td>Demineralized with alkali or acid followed by HNO$_3$/H$_2$O treatment</td>
<td>242</td>
<td>20-78</td>
<td>82.1 (13.8)</td>
<td>-</td>
<td>Lopez et al. (2013)</td>
</tr>
<tr>
<td>Waste bicycle tyre (fine powder)</td>
<td>Pyrolysis in open air</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Methylene blue (10.24)</td>
<td>Jha &amp; Subedi (2011)</td>
</tr>
<tr>
<td>Waste rubber tyre tube (1-3 mm)</td>
<td>Pyrolysis in nitrogen, 60 bars</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Methylene blue (11.51)</td>
<td>Joseph et al. (2015)</td>
</tr>
<tr>
<td>Waste rubber tyre tube (1-3 mm)</td>
<td>Pyrolysis in nitrogen and steam</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Methylene blue (29.43)</td>
<td></td>
</tr>
<tr>
<td>Powder from cryogenic and ambient grinding</td>
<td>Partial carbonization: self-generated atmosphere, 200°C, 15 min</td>
<td>7.52</td>
<td>41.6</td>
<td>12-20 2,4-dichlorophenol</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Powder from cryogenic and ambient grinding</td>
<td>Physical activation: self-generated atmosphere, 500-700°C, 60-120 min Impregnation: ZnCl$_2$, 1:3</td>
<td>15.4</td>
<td>44.9</td>
<td>- 2,4-dichlorophenol</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Powder from cryogenic and ambient grinding</td>
<td>Impregnation: H$_2$PO$_4$, 110°C, 2 h Carbonization: N$_2$, 650°C, 2.5 h</td>
<td>400</td>
<td>-</td>
<td>80-88</td>
<td>-</td>
<td>Belgacem et al. (2013)</td>
</tr>
</tbody>
</table>
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