Rhodamine B dyes adsorption on palm kernel shell based activated carbons

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INTRODUCTION

Materials that are rich in carbon content and do not fuse in carbonization can be the precursor of activated carbon (AC). Factors to be considered in the selection of AC precursor include high carbon content, low ash content, high density, sufficient volatile content, sustainable supply and inexpensiveness. Agricultural by-products such as coconut shell, fruit stone, palm kernel shell (Lee and Zaini, 2015; Hidayu and Muda, 2016), oil palm empty fruit bunch (Osman et al., 2016), palm frond (Ahmad et al., 2015) and palm trunk (Pal et al., 2017) are potential precursors of AC. These materials have little or no economic value and present a disposal problem to the environment, yet they are rich in carbon content and low ash content for AC production.

Malaysia is the second largest producer of palm oil in the world. The production of crude palm oil in Malaysia is expected about 20 million tonnes in 2017 (Zainul, 2017). In the production of crude palm oil, a large amount of solid waste is also an output of the palm oil industry. For every 10 tonnes of crude palm oil produced during the milling process, 5.2 tonnes of fibre, 2.2 tonnes of shell, 8.5 tonnes of empty fruit bunch and other wastes are generated as well. Malaysia’s palm oil industry in 2015 had generated 88 million tonnes of solid biomass, which includes oil palm frond, oil palm trunk, empty fruit bunch, palm kernel shell and mesocarp fibre. These materials can also be used as renewable energy sources for fuel and electricity (Adilla, 2017).

About 5.61 million tonnes of palm kernel shell (PKS) are generated annually. Although it has a high heating value of 17 MJ/kg from the viewpoint of renewable energy, it can also be exploited to produce value-added products, such as char, briquette and AC. Furthermore, PKS is less suitable to be utilized as organic fertilizer because of its hard surface structure (Yashim et al., 2016). Due to its abundance, the use of PKS as an adsorbent precursor is expected to greatly reduce the inherent costs and issues revolving around the management of oil palm waste. PKS is a promising candidate of AC precursor due to its granular structure, chemical stability, high mechanical strength and local availability at almost no cost (Panneerselvam et al., 2012). From Table 1, palm kernel shell shows a higher lignin and a lower cellulose content amongst other oil palm wastes, indicating its suitability to be activated into porous carbon in a short time.

Table 1 Composition of some oil palm wastes (Lee and Zaini, 2015).

<table>
<thead>
<tr>
<th>Oil palm waste</th>
<th>Lignin (wt%)</th>
<th>Cellulose (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm kernel shell</td>
<td>44.5</td>
<td>26.7</td>
</tr>
<tr>
<td>Palm empty fruit bunch</td>
<td>13.0-37.0</td>
<td>43.0-65.0</td>
</tr>
<tr>
<td>Palm frond</td>
<td>20.0-21.0</td>
<td>40.0-50.0</td>
</tr>
<tr>
<td>Palm trunk</td>
<td>18.0-23.0</td>
<td>29.0-37.0</td>
</tr>
</tbody>
</table>

Palm kernel shell-based activated carbon

A number of researchers has studied the feasibility of PKS as AC precursor. Table 2 summarizes the recent studies on the preparation and adsorption performance of palm kernel shell-based activated carbons (PKSACs).

Generally, PKS is a promising precursor to produce ACs with specific surface area greater than 1000 m²/g (Hidayu and Muda, 2016; Yacob et al., 2008; Yacon et al., 2009; Ulfah et al., 2016). PKSACs are used to challenge dyes, organic pollutants and heavy metals, of which, the maximum adsorption capacity can be as high as 500 mg/g (Ruiz et al., 2014). Certainly, the adsorption performance is controlled by a number of variables and parameters such as the preparation methods and the physicochemical properties of ACs and adsorbates.
Case study: palm kernel shell-based activated carbon for the adsorption of Rhodamine B

Rationale

About 1.3 million tonnes of dyes are produced and used in textile industry annually. Of these, 10-25 % is lost during the dyeing process and 2-20 % is discharged as effluent. In other words, nearly 260,000 tonnes of dyes are lost to the effluent every year due to the inefficiency of the dyeing process. This effluent contributes to dye wastewaters and becomes the major source of pollution problem. The conventional wastewater treatment processes are not sufficient enough to completely remove dyes in water as dyes are highly stable to light, temperature, detergents, chemicals, soap, bleach and perspiration. Consequently, dyes resist biodegradation and remain in the environment for an extended period of time. The major concern with dyes wastewaters is the restricted absorption and reflection of sunlight entering the water that can reduce the photosynthetic activities of aquatic plants and impede their growth, hence affecting the food chain (Abou-Gamra and Medien, 2013). Therefore, it is imperative to treat wastewater laden with dyes.

Rhodamine B (RB) is a cationic dye, which was chosen as an adsorbate model in this case study because it has a strong absorption band in the visible region of 578 nm, with a high stability against pH change. RB or basic violet 10 is a water-soluble cationic dye, which is a common water tracer fluorescent to determine the rate and direction of flow and transport. The IUPAC name of RB is [9-(2-carboxyphenoxy)-6-(diethylamino)xanthene-3-ylidene]-diethylazanium chloride (PubChem, 2005). It is composed of green crystals or reddish-violet powder, and becomes bluish-red colour once dissolved in water. RB can cause irritation to eyes and skin, respiratory as well as gastrointestinal tract. The symptoms after acute exposure to RB include eyes burning and excessive tearing, nasal itching and burning, chest burning, pain and tightness, cough, headache, pruritic skin burns, nausea, rhinorrhea, dyspnoea and throat burning. Most organic azo dyes such as methylene blue, sudan II and RB are water-insoluble azo dyes. Occupational contact with hair dyes and dyeing textile resins may cause eczematous allergic dermatitis and lichen planus (Shahzad, 2014). The present case study was reported on the evaluation of PKS-AC as a potential adsorbent for RB removal from water. PKS-AC was prepared via ZnCl₂ activation at 600 °C for 2 h. The carbonized palm kernel shell (char) was employed for comparison to show the effect of chemical activation using zinc chloride.

### Table 2: Processing conditions and adsorption performance of PKSACs.

<table>
<thead>
<tr>
<th>AA</th>
<th>IR</th>
<th>Activation</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Gas</th>
<th>Yield (%)</th>
<th>S_{BET} (m²/g)</th>
<th>Qₑ (mg/g)</th>
<th>Adsorbate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>2</td>
<td></td>
<td>927</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>2</td>
<td></td>
<td>43.3</td>
<td>104</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KOH</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>2</td>
<td></td>
<td>44.5</td>
<td>161</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1</td>
<td>-</td>
<td>700</td>
<td>2</td>
<td>N₂</td>
<td>1082</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KOH</td>
<td>1</td>
<td>400 1</td>
<td>800</td>
<td>0.75</td>
<td>*Limited air/ N₂</td>
<td>127</td>
<td>Methylene blue</td>
<td>3.22</td>
<td>-</td>
<td>Abechi et al. (2013a)</td>
</tr>
<tr>
<td>KOH</td>
<td>2</td>
<td>300 1</td>
<td>700</td>
<td>1</td>
<td>N₂</td>
<td>490</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>Imalerio et al. (2014)</td>
</tr>
<tr>
<td>KOH</td>
<td>2</td>
<td>-</td>
<td>800</td>
<td>-</td>
<td>N₂</td>
<td>810</td>
<td>Carboxylic acid</td>
<td>550</td>
<td>-</td>
<td>Ruiz et al. (2014)</td>
</tr>
<tr>
<td>60% KOH</td>
<td>2</td>
<td>-</td>
<td>800</td>
<td>-</td>
<td>N₂</td>
<td>772</td>
<td>120</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>N₂</td>
<td>41.5</td>
<td>44.4</td>
<td>17.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>N₂</td>
<td>38.6</td>
<td>38.8</td>
<td>72.0</td>
<td>-</td>
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<tr>
<td>Steam</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>0.5</td>
<td></td>
<td>81.4</td>
<td>40.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>3</td>
<td>170 1</td>
<td>500</td>
<td>0.5</td>
<td>Limited air</td>
<td>48.8</td>
<td>1665</td>
<td>β-carotene</td>
<td>14.3</td>
<td>Ulfah et al. (2016)</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>0.5</td>
<td>N₂</td>
<td>500</td>
<td>3.95</td>
<td>1.24</td>
<td>RH-200</td>
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</tr>
<tr>
<td>K₂CO₃</td>
<td>1</td>
<td>-</td>
<td>4</td>
<td>0.5</td>
<td>N₂</td>
<td>600</td>
<td>14.4</td>
<td>4.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PO₄</td>
<td>2</td>
<td>30%</td>
<td>500</td>
<td>1</td>
<td></td>
<td>-</td>
<td>-</td>
<td>Pb²⁺, Cu²⁺</td>
<td>1.25</td>
<td>Vincent et al. (2016)</td>
</tr>
<tr>
<td>KOH</td>
<td>0.5</td>
<td>-</td>
<td>700</td>
<td>1</td>
<td>Limited air</td>
<td>16.8</td>
<td>336</td>
<td>Rhodamine B</td>
<td>5.24</td>
<td>Yong and Zaini (2016)</td>
</tr>
</tbody>
</table>

*AA: activating agent; IR: impregnation ratio; T: temperature in °C; t: time in hour; S_{BET}: specific surface area in m²/g; Qₑ: adsorption capacity in mg/g

*Assumed
RESEARCH STRATEGIES

PKS was obtained from Felda Taib Andak, Kulai, Johor. Rhodamine B dye (RB, C17H11ClN2O2S, MW = 479.22 g/mol and λmax = 578 nm), zinc chloride (ZnCl2, 99.5 %) and hydrochloric acid (HCl, 37.0 %) were supplied by R&M Marketing, Essex, U.K. All chemicals were of analytical-grade reagents.

AC was prepared from PKS by chemical activation using ZnCl2. Raw PKS was crushed and sieved to a size of < 1 mm, and then washed several times with running tap water to remove dirt and impurities. ZnCl2 was mixed with dried PKS at a weight ratio of 1:1 (ZnCl2:PKS). The activating agent was first dissolved in water and the mixture was stirred and homogenized at 90°C for 1.5 h. Upon oven-drying at 110°C, the impregnated PKS was subjected to carbonization in a furnace at 600°C for 2 h. The resultant product, designated as PKS-AC was soaked in 0.1 M HCl overnight to remove excess chemicals. After that, the material was washed with hot distilled water to remove excess minerals and acid to a solution pH of 4. Then, the sample was oven-dried prior to characterization and adsorption. PKS-AC was characterized according to the textural properties using a Pulse ChemiSorb 2705 with liquid N2 at 77 K.

About 0.05 g of PKS-AC was brought into intimate contact with 50 mL of RB solution (pH = 4.1±0.8) of varying concentrations (5 to 400 mg/L). The mixture was allowed to equilibrate on a shaker at 50 mL of RB solution (pH = 4.1±0.8) of varying concentrations (5 to 400 mg/L). The mixture was allowed to equilibrate on a shaker at 30°C for 72 h. The residual concentration was measured by a UV-Vis spectrophotometer (Drawell DU-8200) at a wavelength of 578 nm.

The adsorption capacity was calculated as,

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

where \( Q_e \) (mg/g) is the adsorption capacity, \( C_0 \) (mg/L) is the initial concentration of dye solution, \( C_e \) (mg/L) is the equilibrium concentration of dye solution, \( m \) (g) is the mass of activated carbon and \( V \) (L) is the volume of dye solution.

Four isotherm models were used to analyze the adsorption data (Dada et al., 2012). The Langmuir isotherm as expressed in Equation (2) described the formation of monolayer adsorbate on the outer surface of adsorbent,

\[ Q_e = \frac{Q_max b C_0}{1+ b C_0} \] 

where \( Q_e \) (mg/g) is the equilibrium adsorption capacity of dye by adsorbent, \( C_0 \) (mg/L) is the equilibrium concentration of dye solution, \( Q_max \) (mg/g) is the maximum monolayer capacity of adsorbent, and \( b \) (L/mg) is the Langmuir adsorption constant. The separation factor, \( R_L \) was the essential feature of Langmuir isotherm,

\[ R_L = \frac{1}{1+ b C_0} \] 

where \( C_0 \) (mg/L) in Equation (3) is the maximum initial concentration. The \( R_L \) value represents the adsorption nature either unfavourable (\( R_L \), linear (\( R_L = 1 \)), favourable (0 < \( R_L < 1 \)) or irreversible (\( R_L = 0 \)). The Freundlich isotherm model was applied to the non-ideal, multilayer adsorption on heterogeneous adsorbent surface. The Freundlich equation was given as,

\[ Q_e = K \left( \frac{C_0}{C} \right)^n \] 

where \( K \) and \( n \) are the Freundlich constants. The Redlich-Peterson (RP) isotherm is a combination featuring both Langmuir and Freundlich models. It is applicable for a wide concentration range, either in homogeneous or heterogeneous system. The RP model was described as,

\[ Q_e = \frac{K Q_max C_0}{1+ a Q_max C_0}^\beta \] 

where \( K_R \) (L/g) and \( \alpha_R \) (L/mg)^\beta are the RP isotherm constants, and \( \beta \) is the exponent lies between 0 and 1. The Dubinin-Radushkevich (DR) isotherm is generally applied to describe the adsorption mechanism by Gaussian energy distribution onto a heterogeneous surface. The DR equation was expressed as,

\[ Q_e = Q_s \exp \left( -K_R C_e^{\beta} \right) \] 

where \( Q_s \) (mg/g) is the theoretical isotherm saturation capacity, \( K_R \) (mol^2/kJ^2) is the Dubinin-Radushkevich constant and \( \epsilon \) is the Polanyi potential as expressed in Equation (7),

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

where \( R \) (= 8.314 J/mol. K) is the gas constant and \( T \) (K) is the absolute temperature. The physical adsorption and chemical adsorption are distinguished by the mean free energy, \( E \) per molecule of adsorbate as expressed in Equation (8),

\[ E = -\frac{1}{\sqrt{K_R}} \] 

For instance, the magnitude of \( E \) between 8 and 16 kJ/mol suggests that the adsorption may involve ion exchange reaction.

FINDINGS AND DISCUSSION

Table 3 shows the effect of chemical activation on the yield and textural properties of synthesized materials. PKS-AC displayed a higher yield, suggesting the role of ZnCl2 as superior dehydrating agent to inhibit the formation of tar. The char has a poor surface area (208 m^2/g) compared to PKS-AC (1365 m^2/g) because the pores were not well-developed and blocked with tar. Therefore, PKS-AC yielded a better adsorption performance due to its textural properties.

![Table 3 Textural properties, yield, and rhodamine B adsorption by palm kernel shell char and activated carbon (PKS-AC).](image)

Adsortent | Char | PKS-AC |
--- | --- | --- |
BET surface area (m^2/g) | 208 | 1365 |
Total pore volume (cm^3/g) | - | 0.587 |
Micropore volume (cm^3/g) | - | 0.488 |
Microporosity (%) | - | 83.2 |
Average pore size (nm) | - | 1.89 |
Yield (%) | 33.4 | 51.8 |
Maximum adsorption capacity (mg/g) | 16.3 | 108 |

From Fig. 1, PKS-AC demonstrated an increasing trend of equilibrium adsorption, \( Q_e \) and achieved a saturation point which was known as maximum capacity at 108 mg/g. At a low concentration, the ratio of the initial number of adsorbate molecules to the available active sites (surface area) is low, therefore the equilibrium adsorption is concentration-dependent. At a high concentration, the vacant sites become fewer, thus the amount of equilibrium adsorption is influenced by the available sites. As the concentration increases, the adsorption amount becomes constant and the saturation is achieved (Hema and Arivoli, 2007).

The equilibrium adsorption data was analyzed using four isotherm models. Table 4 summarizes the isotherm constants for the removal of RB by PKS-AC. The Langmuir model showed that the correlation of determination (R^2) was close to 1, indicating its applicability to describe RB adsorption by PKS-AC. The adsorption process was assumed to take place on the homogenous surface of PKS-AC via the formation of monolayer of RB molecules. Furthermore, the n value of Freundlich model was greater than 1 for PKS-AC, indicating that the adsorption obeyed the ordinary Langmuir isotherm. The Langmuir constant, \( b \) was related to the energy of adsorption.
adsorption. It suggested a favourable adsorption at low concentration, which also indicated a high affinity interaction between the active sites on adsorbent surface and the adsorbate molecules. PKS-AC possessed a $R_l$ value in the range 0 to 1, showing that the adsorption was favourable and reversible.

Fig. 1. Equilibrium removal of rhodamine B by PKS-AC. Lines were predicted by Langmuir (dotted), Freundlich (solid), Redlich-Peterson (dashed) and Dubinin-Radushkevich (double solid) models.

The equilibrium adsorption data was analyzed using four isotherm models. Table 4 summarizes the isotherm constants for the removal of RB by PKS-AC.

Table 4 Isotherm constants for RB removal by PKS-AC.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>$Q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
<th>$SSE$</th>
<th>$R_l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>108</td>
<td>0.907</td>
<td>0.976</td>
<td>166</td>
<td>0.002</td>
</tr>
<tr>
<td>Freundlich</td>
<td>7.80</td>
<td>53.0</td>
<td>0.780</td>
<td>1447</td>
<td></td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>K ($L/g$)</td>
<td>$\beta$</td>
<td>$a_n$ (L/mg)$^b$</td>
<td>$R^2$</td>
<td>$SSE$</td>
</tr>
<tr>
<td></td>
<td>98.1</td>
<td>0.943</td>
<td>1.20</td>
<td>0.986</td>
<td>166</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$K_d$ (mol$^2$/kJ)$^2$</td>
<td>$Q_s$ (mg/g)</td>
<td>$R^2$</td>
<td>$E$ (kJ/mol)</td>
<td>$SSE$</td>
</tr>
<tr>
<td></td>
<td>1.73 x 10^{-2}</td>
<td>0.968</td>
<td>1.70</td>
<td>208</td>
<td></td>
</tr>
</tbody>
</table>

The Redlich-Peterson isotherm is a hybrid of Langmuir and Freundlich models. From Table 4, the Redlich-Peterson constant, $\beta$ approached unity and agreed well with the Langmuir isotherm. From the Dubinin-Radushkevich isotherm, $E$ is the mean free energy of adsorption, and it was assumed that $E < 8$ kJ/mol was due to physical adsorption (Jeyaraj et al., 2014). Also, the $Q_s$ value of Dubinin-Radushkevich model was close to $Q_{DL}$ value of Langmuir model. The values of sum of the squared error (SSE) of Langmuir and Redlich-Peterson models were the lowest, indicating the best fit of the equilibrium data by these models.

CONCLUSION

Palm kernel shell is a promising precursor of AC with specific surface area greater than 1000 m$^2$/g. This paper highlighted the promising role of palm kernel shell-based activated carbons in the removal of water pollutants. In the case study, ZnCl$_2$-activated palm kernel shell carbon showed a high surface area of 1365 m$^2$/g with the maximum adsorption of rhodamine B of 108 mg/g.

ACKNOWLEDGEMENT

The authors would like to express their appreciation to Universiti Teknologi Malaysia for the award of tier 1 UTM-RUG no.18H50 and UTM Zamalah scholarship.

REFERENCES


