Porous structure and adsorptive properties of hide waste activated carbons prepared via potassium silicate activation

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Abstract

A novel activating agent, potassium silicate, was employed in the preparation of hide waste activated carbon. Effects of different activation temperatures and impregnation ratios on porous activated carbon evolution were evaluated by nitrogen adsorption/desorption. The BET specific surface area and pore volume of prepared activated carbon could attain 2046.12 m\textsuperscript{2}/g and 1.068 cm\textsuperscript{3}/g, when the process of preparation carried out at the best conditions (activation temperature of 700\textdegree{}C and the impregnation ratio of 2:1).

Methylene blue (MB) was selected as the adsorbate to evaluate its adsorption property. Adsorption results can be fitted well by the Langmuir isotherm, indicating the maximum monolayer adsorption capacity of MB reached to 769.23mg/g.

Keywords: Activated carbon; Potassium silicate; Hide waste; Methylene blue
1. Introduction

Activated carbon, the most common and effective adsorbent, has large specific surface area, complex aperture structure and variety of functional groups, which can be prepared by any carbonaceous materials. Today, waste materials such as macadamia nut endocarp [1], lotus stalk [2], waste tires [3] etc. are transformed into activated carbons, which has become one of the research focuses. When raw hide and skin convert into leather, solid and liquid wastes would produce. The solid waste such as hide waste (HW) had keratin ingredient which was often discarded due to the low economic benefits, thus the reasonable application of this solid waste should be studied further. Nevertheless, according to the literature, there is little information about the preparation of activated carbon from HW.

There are two main activation methods in the preparation of activated carbon, namely physical and chemical methods. As to chemical method, KOH, NaOH, H\textsubscript{3}PO\textsubscript{4} and ZnCl\textsubscript{2} were often used as the activating agents [4]. The carbon produced by KOH or NaOH generally has microporous structure, whereas KOH or NaOH can corrode apparatus whose life would be shortened and thus limit the development and application of this activating agent. Actually, silicone material is widely used as flame retardants in the field of extinguishing as a result of hindering the combustion of materials from originating [5]. However, to our knowledge, there are no papers using potassium silicate (K\textsubscript{2}SiO\textsubscript{3}) as the activating agent for preparing activated carbon. The purpose of this study was to prepare hide waste activated carbon (HWAC), using K\textsubscript{2}SiO\textsubscript{3} as the activating agents to evaluate the pore structure and adsorption properties.
2. Materials and methods

2.1. Preparation of activated carbons

HW was provided by a tanning industry from Shandong province in China. The raw material was first soaked with ethanol for 48 h to remove some fat, then washed and dried at 60 °C. The dried materials were cut into particles of 0.5 cm × 0.5 cm, then dipped with a certain concentration of K$_2$SiO$_3$ solution to a varying impregnation ratio of 1:1–3:1 (R, g K$_2$SiO$_3$/g HW). After impregnation for 12 h, the mixtures were heated at 105 °C for 30 min to evaporate some of water. Samples were heated to the desired temperatures (400, 500, 600, 700, and 800 °C) in a tube furnace, and maintained for 1 h under a stable nitrogen flow (100 mL/min). The products were washed with hot water and distil water to ensure the pH of washing liquid attained neutral, and then dried at 105 °C for 12 h. Finally, the desired carbons were sieved to a particle size of 0.076–0.15 nm, and stored in a desiccator for the next study.

2.2. Characterization of HW-K$_2$SiO$_3$ and HWAC

The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of HW after K$_2$SiO$_3$ impregnated were acquired by an SDT-simultaneous TGA–DTA model, which were performed in pure N$_2$ atmosphere (100 mL/min). The mixture was heated at the heating rate of 10 °C from room temperature to 700 °C, and held this temperature for 1 h. The BET specific surface area ($S_{BET}$) and pore size distribution of HWACs were characterized using a surface area analyzer (JW-BK122W, China) by N$_2$ adsorption–desorption isotherm at 77 K. The surface morphology of activated carbon was determined by scanning electron microscopy (SEM) (HitachiS-520, Japan).
2.3. Equilibrium adsorption experiment

Activated carbon under the conditions of the activated temperature of 700 °C and the impregnation ratio of 2:1 with the highest $S_{BET}$ (AC) was selected to perform the adsorption experiments. Batch experiments were conducted in a series of 150-mL conical flasks containing 50 mL MB and 0.05 g adsorbents with different initial concentrations ranging from 75 to 900 mg/L. The flakes were placed in a thermostatic shaker (SHA-B, Shanghai, China) and shaken at 25 °C with a speed of 160 rpm for 24 h to ensure the equilibrium. Finally, the concentrations of MB solution after filtrating were determined by a UV–vis spectrophotometer (UV-754, Shanghai) at $\lambda_{max} = 665$ nm. Blank experiments without adsorbents were also performed as described above. The adsorption isotherm experiments were carried out in duplicate and the mean value was reported. The adsorption capacity, $q_e$ (mg/g), could be calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

(1)

where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations of MB solutions. $V$ (L) is the solution volume of MB solutions. $W$ (g) is the mass of activated carbon.

2.4. Equilibrium modeling

The equilibrium data of MB adsorption were modeled using Langmuir [6] and Freundlich [7] equations as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

(2)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(3)

where $q_m$ and $q_e$ (mg/g) are the maximum and the equilibrium adsorption capacities, respectively. $K_F$ (L/mg) is the Langmuir constant related to the free energy of
adsorption. \( K_F \) (mg/g) \((L/mg)^{1/n}\) and \( n \) are the Freundlich constants associated with adsorption intensity.

3. Results and discussion

3.1. Characterization of HW-K\(_2\)SiO\(_3\) and HWAC

3.1.1. Thermogravimetric analysis of HW-K\(_2\)SiO\(_3\)

The TGA and DTG curves of HW-K\(_2\)SiO\(_3\) are shown in Fig. 1. TGA profile shows that the process of weight loss contained three sections. The weight loss in the first 20 min could be due to the water evaporation and the degeneration of keratin, reflected in the DTG curve two small peaks. The second stage occurred between 20 min and 45 min, which attributed to the volatile of organic matter and moisture. The peaks at the temperatures of 287 °C and 450 °C in the DTG curve were corresponded with the thermal decomposition of denatured proteins under the catalysis of silicate. After 40 min, the weight loss decreased slightly, illustrating that the catalytic action of K\(_2\)SiO\(_3\) completed.

![TGA and DTG curves for the pyrolysis of HW-K\(_2\)SiO\(_3\).](image)
3.1.2. Nitrogen adsorption behavior and porosity development

The N\textsubscript{2} adsorption/desorption isotherms and pore size distributions of the prepared activated carbons under different conditions are shown in Fig. 2. The N\textsubscript{2} adsorption/desorption isotherms reflected different adsorption capacities of nitrogen and hysteresis loops, indicating the appearance of mesopores and presence of majority micropores (AC). The N\textsubscript{2} adsorption/desorption curves were mixture of type I and type IV isotherms [8], illustrating the pores of the carbons were micropores and mesopores. Table 1 shows the BET surface areas, pore volumes, and average pore sizes of the prepared activated carbons. It can be concluded that HW and K\textsubscript{2}SiO\textsubscript{3} were excellent precursor and activating agent respectively in the preparation of activated carbon. \(S_{\text{BET}}\) first increased then decreased with the activated temperature, and it showed the same trend with the impregnation ratio. This may be attributed to high activation energy between carbon atom and K\textsubscript{2}SiO\textsubscript{3}. Consequently, under the conditions of the activated temperature of 700 °C and the impregnation ratio of 2:1, HWAC had the highest specific surface area (2046 m\textsuperscript{2}/g) and total pore volume (1.068 cm\textsuperscript{3}/g). Table 1 also reflects that the high proportion of micropores was beneficial to the high specific surface area, and the majority of pore size was micropores and mesopores. The pore sizes distribution (Fig. 2) reveals that most of the pores ranged around 2 nm, which indicates the activated carbons had micro–mesopores structure, corresponding to the N\textsubscript{2} adsorption/desorption results.
Fig. 2. Effects of (a) activating temperature (preparation condition: $R = 2:1$; activating time = 1 h), (b) impregnation ratio (activating temperature = 700 °C; activating time = 1 h) on pore size distributions and nitrogen adsorption/desorption isotherms (inset) for HWAC.
Table 1
The effect of activation temperature and impregnation ratio on BET surface areas, pore volumes, average pore sizes of activated carbons activated by K$_2$SiO$_3$.

<table>
<thead>
<tr>
<th>Activated temperature (°C)</th>
<th>R</th>
<th>$S_{\text{BET}}$</th>
<th>$S_{\text{mic}}$ ($\text{m}^2/\text{g}$)</th>
<th>$S_{\text{mic}}/S_{\text{BET}}$</th>
<th>$V_{\text{tot}}$ ($\text{cm}^3/\text{g}$)</th>
<th>$V_{\text{mic}}$ ($\text{cm}^3/\text{g}$)</th>
<th>$V_{\text{mic}}/V_{\text{tot}}$ (%)</th>
<th>$D_{p}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2:1</td>
<td>7.93</td>
<td>0.318</td>
<td>4.01</td>
<td>0.071</td>
<td>0.0025</td>
<td>3.52</td>
<td>35.89</td>
</tr>
<tr>
<td>500</td>
<td>2:1</td>
<td>716.69</td>
<td>0.318</td>
<td>4.01</td>
<td>0.071</td>
<td>0.0025</td>
<td>3.52</td>
<td>35.89</td>
</tr>
<tr>
<td>600</td>
<td>2:1</td>
<td>1071.8</td>
<td>697.21</td>
<td>88.07</td>
<td>0.436</td>
<td>0.3371</td>
<td>77.32</td>
<td>2.20</td>
</tr>
<tr>
<td>700</td>
<td>2:1</td>
<td>2046.1</td>
<td>1803.20</td>
<td>88.13</td>
<td>1.068</td>
<td>0.8103</td>
<td>75.87</td>
<td>2.09</td>
</tr>
<tr>
<td>800</td>
<td>2:1</td>
<td>175.05</td>
<td>1115.70</td>
<td>89.56</td>
<td>0.653</td>
<td>0.5054</td>
<td>77.40</td>
<td>2.10</td>
</tr>
<tr>
<td>700</td>
<td>1:1</td>
<td>716.69</td>
<td>616.38</td>
<td>86.00</td>
<td>0.585</td>
<td>0.2961</td>
<td>50.62</td>
<td>3.27</td>
</tr>
<tr>
<td>700</td>
<td>1.5:1</td>
<td>1245.7</td>
<td>616.38</td>
<td>86.00</td>
<td>0.585</td>
<td>0.2961</td>
<td>50.62</td>
<td>3.27</td>
</tr>
<tr>
<td>700</td>
<td>2.5:1</td>
<td>954.51</td>
<td>495.09</td>
<td>83.28</td>
<td>0.399</td>
<td>0.2435</td>
<td>61.03</td>
<td>2.69</td>
</tr>
<tr>
<td>700</td>
<td>3:1</td>
<td>333.34</td>
<td>91.87</td>
<td>27.56</td>
<td>0.644</td>
<td>0.1301</td>
<td>20.20</td>
<td>7.72</td>
</tr>
</tbody>
</table>

a $S_{\text{BET}}$: BET specific surface area.

b $S_{\text{mic}}$: micropore specific surface area.

c $V_{\text{tot}}$: total pore volume.

d $V_{\text{mic}}$: micropore volume.

e $D_p$: the mean pore.

Table 2 shows the element contents of C, N, O, S, and Si of HW and AC. It can be seen that both of HW and AC had high content of C, N, O, and S but low Si content. HW contains the protein substance, which explained the higher contents of N, S, O for HW than AC, but the content of C increased after activation.

Table 2
Elemental change between HW and AC.

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Si (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>65.69</td>
<td>18.55</td>
<td>13.51</td>
<td>2.25</td>
<td>0</td>
</tr>
<tr>
<td>AC</td>
<td>87.15</td>
<td>6.05</td>
<td>6.76</td>
<td>0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>
SEM micrographs of AC (Fig. 3) shows that the prepared activated carbon had a smooth surface and highly developed pores. It is indicated that K$_2$SiO$_3$ favored for the generation of porous structure. K$^+$ could transform into elemental potassium, thus massive pores produced [9].

![SEM micrographs of AC at different magnifications (2000× and 7000×).](image)

3.2. MB adsorption analysis

The adsorption properties of AC were evaluated by MB adsorption to test its adsorption performance. Table 3 shows that Langmuir isotherm was more suitable to describe the adsorption with high correlation coefficient ($R^2 = 0.9999$), indicating monolayer coverage of MB molecules and uniform energy. The comparisons of specific surface area and maximum monolayer adsorption capacity of various adsorbents are displayed in Table 4. Compared with the previous study, AC in this work showed high MB adsorption capacity (769.23 mg/g) which was much higher than that of the other adsorbents prepared from other materials and different activating agents. According to the results, AC as an excellent adsorbent could be
applied in the removal of dye in wastewater. Hence, HW and K₂SiO₃ were preferable raw material and activating agent in the process of activated carbon preparation.

Table 3
Langmuir and Freundlich isotherm constants for the adsorption of MB onto AC.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_m (mg/g)</td>
<td>K_L a (L/mg)</td>
</tr>
<tr>
<td>769.23</td>
<td>14.44</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

a K_L: Langmuir constant.
b K_F: Freundlich constants which relate to the adsorption capacity.
c n: Freundlich constants which relate to the adsorption capacity intensity.

Table 4
Comparisons of BET specific surface area and MB adsorption capacity of various adsorbents.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Activating agent</th>
<th>S_BET (m²/g)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husks</td>
<td>KOH</td>
<td>752</td>
<td>362.6</td>
<td>[10]</td>
</tr>
<tr>
<td>Jatropha curcas fruit shell</td>
<td>NaOH</td>
<td>1873</td>
<td>499.17</td>
<td>[11]</td>
</tr>
<tr>
<td>Rice husks</td>
<td>K₂CO₃</td>
<td>1165</td>
<td>441.52</td>
<td>[10]</td>
</tr>
<tr>
<td>Peach stones</td>
<td>H₃PO₄</td>
<td>1298</td>
<td>412</td>
<td>[12]</td>
</tr>
<tr>
<td>Black liquor lignin</td>
<td>Steam</td>
<td>310.15</td>
<td>92.51</td>
<td>[13]</td>
</tr>
<tr>
<td>Cocoa shell</td>
<td>CO₂</td>
<td>85.09</td>
<td>212.77</td>
<td>[14]</td>
</tr>
<tr>
<td>Walnut shells</td>
<td>ZnCl₂</td>
<td>1800</td>
<td>315</td>
<td>[15]</td>
</tr>
<tr>
<td>Leather waste</td>
<td>H₄P₂O₇</td>
<td>638.57</td>
<td>303.03</td>
<td>[16]</td>
</tr>
<tr>
<td>Hide waste</td>
<td>K₂SiO₃</td>
<td>2046</td>
<td>769.23</td>
<td>In this study</td>
</tr>
</tbody>
</table>

4. Conclusion

This study highlighted the potential of potassium silicate and hide waste as the efficient activating agent and raw precursor for preparation of activated carbon, respectively. The prepared carbon possessed BET specific surface area as 2046.12 m²/g and total pore volume as 1.068 cm³/g at the best condition (T = 700 °C, R = 2:1). K₂SiO₃ activation enhanced the development of aperture and benefited the production of micro–mesopores carbon. The
adsorption isotherm results fitted the Langmuir equation with the monolayer adsorption capacity for MB of 769.23 mg/g.

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References


