Effect of Supercritical Water Treatment on Porous Structure of Activated Carbon
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ABSTRACT

Recently supercritical water has been recognized as a potentially powerful method for the regeneration of spent activated carbon. Unlike thermal regeneration, supercritical water reaction decomposes the unwanted adsorbate but mildly oxidize the carbon, thereby causing little regeneration losses. However, it is likely that some porous properties and adsorption capacity might change during regeneration with supercritical water. The main purpose of this work is to investigate the effect of supercritical water treatment on the porous structure of three kinds of activated carbon: a commercial activated carbon (CAL carbon), activated carbon made from waste tire rubber, and activated anthracite. The porous characteristics of the activated carbons, namely, the micropore volume, mesopore volume and pore size distribution, will be determined from N₂ adsorption-desorption isotherm measured at 77 K with the BET surface area analyzer. In addition, the effect of hydrogen-peroxide promoted supercritical water oxidation on the porous structure will also be studied.

KEYWORDS
Activated carbon, Surface modification, Supercritical water

INTRODUCTION

At present, Thailand imports a large amount of anthracite coal from Vietnam and Laos. It is consumed in many industries such as: Steel Manufacture, Battery Covers Manufacture, Water Filtration Industry, Glass Manufacture, etc. Raw anthracite from the mines usually comes in different shapes and sizes. Imported anthracite goes through various processes include separating, grinding, size classification, and polishing. These processes and its transportation generate a large amount of medium to fine anthracite powder. The fine powder is not only useless but also poses health hazard. Thus it is attractive to turn the anthracite powder into useful products.

Supercritical water reaction is one kind of hydrothermal treatment but carried out above the critical conditions of water. We have found it to be a new efficient method for regenerating spent activated carbons. Besides, the treatment is anticipated to slightly increase the adsorption capacity of the regenerated activated carbon, thanks to the opening of some originally obstructed pores.

The main purpose of this work is to investigate the effect of supercritical water treatment on the porous structure of three kinds of activated carbon: a commercial activated carbon (CAL carbon), activated carbon made from waste tire rubber, and activated anthracite powder.
EXPERIMENTAL

1. Preparation of activated carbon

Three kinds of activated carbons: commercial activated carbon (Calgon, USA.), activated carbon from waste tires rubber and activated carbon from anthracite powder were used as starting materials. About 1 g of each activated carbon and the calculated amount of water were placed in a batch stainless tube reactor and inserted in a tubular furnace. The furnace was electrically heated from room temperature to 400°C with a heating rate of 5°C/min, then held at this temperature for 15 minutes. At this temperature the water inside the tubular reactor completely vaporized and the content was pressurized to 2500 kPa and left to naturally cool down.

2. Characterization of activated carbon

The samples were filtered and dried overnight at 110°C. The samples were weighed to measure the treatment yield and then characterized by N₂ adsorption. The BET surface areas $S_{BET}$, mesopore volume $V_{MESO}$, micropore volume $V_{MICRO}$ and pore size distribution of each sample were determined from the N₂ adsorption-desorption isotherms measured at 77K using the adsorption apparatus (AUTOSORB-1-C, Quantachrome, USA.). Pore size distribution and $V_{MESO}$ were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate $V_{MICRO}$.

RESULTS AND DISCUSSION

Porous properties of activated carbons after supercritical water treatment

The three kinds of activated carbons were treated with supercritical water in the absence and presence of hydrogen peroxide solution and their porous properties after treatment were obtained. The major advantages of supercritical treatment are high yield of regenerated activated carbons and short treatment time. In the presence of hydrogen peroxide solution, supercritical water oxidation might also occur.

Figure 1 shows an example of the N₂ adsorption-desorption isotherms of activated anthracite before and after either supercritical water reaction or supercritical water oxidation. Similarly, Fig. 2 shows an example of the pore size distribution of the activated anthracite before and after treatment.
Table 1 summarizes the porous properties of the three activated carbons before and after treatment. We see that $S_{BET}$, $V_{micro}$ and $V_{meso}$ values of the activated anthracite and activated carbon from waste tires become 2 – 5 % higher after treatment with supercritical water reaction. Possibly, water at 400°C and 3600 kPa has high solubilizing capacity, thereby cleaning out some originally obstructed pores. Another possibility is the supercritical pressure might give rise to microfissure, thereby facilitating access to the closed pores (F. Salvador, C. Sanchez Jimenez, 1999). However, we found insufficient evidence to assert that supercritical water reaction significantly improve the porous properties of the activated carbons.

When hydrogen peroxide is present, the activated carbons are oxidized. $S_{BET}$ values of apparently three activated carbons decrease in Table 1 with the exception of HCAL. This phenomenon occurred at a fast oxidation rate. Alternatively, it may be considered that the surface of the activated carbon was oxidized in whole layers, whereas in steam activation some surface carbons were oxidized. In any case, HCAL still have $S_{BET}$ value similar to the original carbon thanks to the orderly structure of CAL carbon.
Table 1 Porous properties and yield of the 3 activated carbons before and after treatment with either supercritical water reaction or supercritical water oxidation. Treatment conditions are 400°C, 3600 kPa and 15 minutes.

<table>
<thead>
<tr>
<th>Properties</th>
<th>CAL</th>
<th>WCAL</th>
<th>HCal</th>
<th>AA</th>
<th>WAA</th>
<th>HAA</th>
<th>WT</th>
<th>WWT</th>
<th>HWT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{BET} ) (m(^2)/g)</td>
<td>820</td>
<td>778</td>
<td>792</td>
<td>679</td>
<td>691</td>
<td>321</td>
<td>641</td>
<td>669</td>
<td>51</td>
</tr>
<tr>
<td>( V_{Meso} ) (cm(^3)/g)</td>
<td>0.19</td>
<td>0.20</td>
<td>0.28</td>
<td>0.08</td>
<td>0.12</td>
<td>0.14</td>
<td>0.45</td>
<td>0.49</td>
<td>0.09</td>
</tr>
<tr>
<td>( V_{Micro} ) (cm(^3)/g)</td>
<td>0.38</td>
<td>0.35</td>
<td>0.35</td>
<td>0.30</td>
<td>0.32</td>
<td>0.13</td>
<td>0.25</td>
<td>0.27</td>
<td>0.001</td>
</tr>
<tr>
<td>( V_{Total} ) (cm(^3)/g)</td>
<td>0.58</td>
<td>0.55</td>
<td>0.63</td>
<td>0.38</td>
<td>0.44</td>
<td>0.27</td>
<td>0.70</td>
<td>0.76</td>
<td>0.1</td>
</tr>
<tr>
<td>( V_{Meso}/V_{Total} )</td>
<td>0.33</td>
<td>0.36</td>
<td>0.44</td>
<td>0.21</td>
<td>0.27</td>
<td>0.52</td>
<td>0.64</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>-</td>
<td>85.90</td>
<td>28.62</td>
<td>-</td>
<td>95.89</td>
<td>45.73</td>
<td>-</td>
<td>91.20</td>
<td>16.74</td>
</tr>
</tbody>
</table>

AC. = Activated carbon
CAL = Commercial activated carbon (CAL carbon)
AA= Activated anthracite
WT= Activated carbon from waste tires
Prefix “W” = Supercritical water reaction
Prefix “H” = Supercritical water oxidation promoted by hydrogen peroxide solution (H\(_2\)O:H\(_2\)O\(_2\); 1:1)

CONCLUSIONS

The supercritical water reaction has shown great potential for the regeneration of activated carbon from waste tires and activated anthracite. The yields were 91 and 96 %, respectively. Meanwhile, their \( S_{BET} \) increased by 5 to 2 %, respectively. When supercritical water oxidation was carried out with the aid of liquid hydrogen peroxide, the reaction occurred too fast and the resulting yields became unacceptable. We are now investigating the effect of the hydrogen peroxide concentration and the actual adsorption characteristics of the above regenerated activated carbons.
NOMENCLATURES

AC         Activated carbon
CAL        Commercial activated carbon (CAL carbon)
AA         Activated anthracite
WT         Activated carbon from waste tires
Prefix “W” Supercritical water reaction
Prefix “H” Supercritical water oxidation promoted by hydrogen peroxide solution (H\textsubscript{2}O:H\textsubscript{2}O\textsubscript{2}; 1:1)
P/P\textsubscript{0}  Relative pressure [-]
Q          The amount of N\textsubscript{2} adsorbed [cm\textsuperscript{3} (STP)/g]
R\textsubscript{p}  Pore radius [nm]
dV\textsubscript{p}/dlog(R\textsubscript{p})  Pore size distribution [cm\textsuperscript{3}/g]
V\textsubscript{meso}  Mesopore volume [cm\textsuperscript{3}/g]
V\textsubscript{micro}  Micropore volume [cm\textsuperscript{3}/g]
S\textsubscript{BET}  BET surface area [m\textsuperscript{2}/g]

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