Preparation of High-Specific Surface Area-Activated Carbon with Oil-Bearing Mud Residue

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ABSTRACT: Oil-bearing mud residue is a hazardous waste composed of minerals, mineral oil, and water. It is characterized by a high yield and a high content of heavy oil. It is not comprehensively utilized and is difficult to process. The primary sources are oil sludge and oil sand from petroleum exploration and development and from petrochemical production. Oil-bearing mud residue is declared a hazardous waste by Chinese law. Thus, its treatment and application is a problem requiring an immediate solution for petroleum and petrochemical industries. Using oil-bearing mud residue as feedstock and NaOH as the activator this study demonstrates production of activated carbon with high specific surface area. Features of this activated carbon include a specific surface area up to 2,700 m²/g and even pore size. Average pore size is less than 2 nm and total pore volume exceeds 2 cm³/g. This method provides a new approach for recycling oil-bearing mud residue.

INTRODUCTION

As an active absorbent material, activated carbon is used widely and in great demand. However, specific surface area and total porous volume of conventional activated carbon are usually 800–1,500 m²/g and 0.5–1.0 cm³/g, respectively, and are far below demands for environmental protection. Currently, activated carbon with high specific surface area is used as an energy storage medium for hydrogen, natural gas, and electricity; as electrode material for electrochemical capacitors; as an efficient adsorption agent for poisonous gases; as a filler for chromatographic columns; as catalyst carriers, and more in cases where conventional activated carbon is not sufficient. Consequently, research and development into high-specific surface area-activated carbon processes have increasingly attracted attention from scientific and technical researchers [1,2,3,4]. Developed countries such as Japan and the United States have successfully produced activated carbon with a specific surface area of more than 2000 m²/g at a price of 85–1 million RMB/ton with petroleum coke and coal tar as feedstocks. Its demand in China depends primarily on import availability. In addition, research into preparation of this material is still in the early stages of experimentation and investigation. Feedstocks include petroleum coke, coconut shell, bamboo, and more [5,6,7]. Preparation of high specific surface area-activated carbon using oil-bearing sludge as a feedstock has not been published in literature around the world.

Oil-bearing mud residue is a hazardous waste. Its primary components are minerals, mineral oil, and water. Characterized by a high yield, high content of heavy oil, it is less comprehensively utilized and difficult to process [8,9]. Its primary source is oil sludge and oil sand from petroleum exploration and development and from the petrochemical production industry. Using oil-bearing mud residue as feedstock and NaOH as the activator a method is provided to produce activated carbon with high specific surface area. This method both disposes of oil sludge and re-uses waste.

EXPERIMENTS

Experimental Materials and Instruments

This study analyzes the reaction of oil-bearing mud residue and A.R. level NaOH from the Beijing Chemical Plant. Experimental instruments employed include an SRJX-4-13 box resistance furnace (Beijing ever light medical equipment Co, LTD), an indoor static pyrolysis oven (constructed on-site), a Quantax 200× Flash 5000–10× X-ray energy spectrometer (FEI Hong Kong, LTD), a Quanta 250 scanning electron mi-
croscope with a tungsten filament (Bruker AXS Corporation, Germany), a NOVA-2000e fully automatic specific surface and porosity analyzer (Quantachrome, USA), and a STA449F3 simultaneous thermal analyzer (NETZSCH-Gerätebau GmbH, Germany).

**Experimental Procedure**

High-specific surface area-activated carbon is prepared using airtight dry distillation and high-temperature activation. Experiment procedures were as follows:

1. The oil-bearing mud residue is mechanically dehydrated.
2. At a specified temperature and under a nitrogen barrier, the dehydrated residue is dry-distilled at a carbonizing temperature of 320–500°C.
3. The carbide is de-ashed to remove its ash content.
4. The de-ashed carbide is mixed with the activator, and the mixture is activated at 320–900°C under the nitrogen barrier.
5. The activated products are ground, washed to neutral and dried at 120°C.

**Sample Characterization**

After desorption at 150°C and 1.33 Pa in the surface area and porosity automatic analyzer (NOVA-2000e) for 4 hrs. The N\(_2\) adsorption isotherm of the sample is measured. Then, specific surface area and pore size distribution are determined using the BET method. Sample components are analyzed qualitatively with assistance of 200× Flash 5000-10× X-ray spectroscopy. The microstructure of the sample was viewed using a Quanta 250 scanning electron microscope in tungsten filament mode.

**RESULTS AND DISCUSSION**

**Effect of Preparation Parameters on the Performance of Activated Products**

Preparation of activated carbon can be divided into two stages: (1) Carbonization of feedstock. The purpose of carbonization is to obtain carbonized material with an initial porosity and mechanical strength. This material is suitable for activation which is virtually pyrolysis of the organic matter in the feedstock including thermal decomposition and polycondensation [10] and (2) Activation of the carbonized material. This is the key process during preparation of activated carbon. It is a series of complex chemical reactions between the activator and carbonized material. Activation is characterized by formation of new pores based on initial pores, extension of the initial pores, and merging and connection between pores [11]. Effects of carbonization of feedstock and activation parameters on performance of activated products are discussed below.

**Influence of Carbonization Temperature**

Composition of oil-bearing mud residue is complicated. Analyses of mud residue from oilfields display the following ranges (W/W) in composition: 15–30% oil, 60–70% water, and 10–15% residue. Preparation of activated carbon requires a set carbonization temperatures. Thus, water, organic matter, and volatile matter in residue may be removed during carbonization resulting in carbonized material with an initial porosity and mechanical strength ready to be activated. The thermal gravimetric curve of the oil-bearing sludge from an oilfield is obtained by a STA449F3 simultaneous thermal analyzer as displayed in Figure 1.

Data in Figure 1 display that the process of carbonization occurs in three stages: volatilization of water and light oil (40–140°C), thermal decomposition (140–410°C), and polycondensation (410–500°C). When temperature exceeds 500°C, the weight loss of feedstock is small indicating the carbonization process stops. Change of iodine adsorption in carbide as a function of carbonization temperature is displayed in Table 1.

Data in Table 1 show that when the carbonization
temperature exceeds 500°C, despite slight decrease in carbon content, the iodine adsorption value is dramatically reduced. This implies that an increase in carbonization temperature will damage the internal structure [12], affect initial pore formation, and reduce adsorption performance. Therefore, appropriate carbonization temperature must be determined for each type of oil-bearing mud residue.

### Effects of Activation Heating Mode

Activation heating modes tested are as follows:

(a) Continuous heating from room temperature to activation temperature (i.e., feedstock is placed into pyrolysis furnace at room temperature);

(b) Rapid heating from room temperature to activation temperature (i.e., feedstock is placed directly into high temperature pyrolysis furnace); and

(c) Pre-activation at low temperature and activation at high temperature. After one hour activation at 800°C \([m(\text{NaOH})/m(\text{C}) = 2]\) the effect of the heating mode on specific surface area of the activated product is measured. Results are displayed in Table 2.

Data in Table 2 show that activation mode (c) is the only method that yields a product with high specific surface area and good data stability and repeatability. That is because the rapid heating of modes (a) and (b) cause the NaOH to dehydrate rapidly. The system then expands causing uneven thermal conductivity. Thus, the activator and carbide cannot fully contact to react well leading to poor repeatability and low specific surface area. Before heating to activation temperature mode (c) pre-activates at 320°C and the activated product has good repeatability and reliability. It may be because 318°C is the melting point of NaOH, such that NaOH is completely dehydrated and the reactants are well distributed. Thus, no expansion phenomenon occurs at that point.

### Influence of Activation Temperature

Using the condition \(m(\text{NaOH})/m(\text{C}) = 2\) and activating for 1 hr, the relation curve between temperature and specific surface area of activated carbon is displayed in Figure 2.

Optimum activation temperature is approximately 800°C as displayed in Figure 2. If the activation temperature is too low the activation reaction cannot be completed and if it is too high the reaction will be excessively aggressive causing pore walls to burn to the point of collapse and thus reducing specific surface area. Therefore, there is an optimal temperature for activating this reaction.

### Influence of Activation Time

Effect of activation time on specific surface area of activated carbon for conditions \(m(\text{NaOH})/m(\text{C}) = 2\) and activation temperature 800°C was analyzed. Results are displayed in Figure 3.

The optimal activation time is approximately 1 hr. As the activation time increases, the specific surface area of activated carbon first increases and then decreases.

### Table 1. Effect of Carbonization Temperature on Adsorption Performance of Carbide.

<table>
<thead>
<tr>
<th>Carbonization Temperature (°C)</th>
<th>Carbide</th>
<th>Carbon Content, w%</th>
<th>Iodine Adsorption, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td></td>
<td>45.2</td>
<td>300.6</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>46.6</td>
<td>357.4</td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>46.0</td>
<td>291.0</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>45.8</td>
<td>256.3</td>
</tr>
</tbody>
</table>

### Table 1. Effect of Heating Mode on Specific Surface Area of Activation Product.

<table>
<thead>
<tr>
<th>Heating Mode</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First Time</td>
</tr>
<tr>
<td>a</td>
<td>2176</td>
</tr>
<tr>
<td>b</td>
<td>1326</td>
</tr>
<tr>
<td>c</td>
<td>2720</td>
</tr>
</tbody>
</table>

![Figure 2. Effect of activation temperature on specific surface area of activated carbon.](image)
As the reaction time and depth increase, the number of micropores increases before the specific surface area reaches its maximum value. When the specific surface area reaches its maximum, the number of micropores also reaches its maximum. If the activation time is extended past this maximum, the micro-pore walls will fall down, and large numbers of micropores will melt into mesopores and macropores, resulting in a decrease in specific surface area [13].

**Influence of Alkali/Carbon Ratio**

The effect of $m$(NaOH)/$m$(C) on specific surface area of activated carbon at an activation temperature of 800°C for 1 hour is measured and the results are displayed in Figure 4. As $m$(NaOH)/$m$(C) increases, the specific surface area of activated product increases significantly. However, when this ratio reaches 2, the surface area changes slowly and shows a tendency to decrease with continued increase of the ratio. Carbonized material and amorphous carbon in the cracks are activated first, and a microporous structure is formed. As the amount of NaOH increases, both the reaction speed and the number of micropores in the carbonized material increase, thus increasing the specific surface area. As $m$(NaOH)/$m$(C) continues to increase, the reaction between excess NaOH and intervals of the carbon atom layer of the formerly generated microporous structure cause the carbon material to over-ablate and pore size increases; thus, specific surface area decreases slightly.

### Analysis and Discussion of Scanning Electron Microscope (SEM) and Porosity

The micro morphology of the activated carbon surface is viewed using a scanning electron microscope (SEM). The features of its surface morphology before and after activation are displayed in Figures 5 and 6, respectively.
The image displayed in Figure 5 reveals a flaky surface for the oil-bearing mud residue that is nearly free of pores only containing a few cracks. The picture of the activated carbon sample displayed in Figure 6, however, shows abundant pore structures on the surface of the particles. Only large pores can be seen, but the large pores provide the necessary sites for the numerous internal micro-pore structures in the activated carbon whose existence are proven by the adsorption characteristics of the activated product displayed in Table 3. Compared with conventional commercial activated carbon, activated carbon prepared in this manner performs better both in specific surface area and poressedness distribution. The conclusion is that the carbonized oil-bearing mud residue is corroded and abundant pore structures are formed through a redox process [14,15,16].

**CONCLUSIONS**

Using oil-bearing mud residue as feedstock and NaOH as the activator, activated carbon with a specific surface area up to 2,780 m²/g was prepared for specific conditions of activation mode, m(NaOH)/m(C) ratio, activation temperature, and activation time. This product has a high percentage of micropores, low average pore size, and large specific surface area. This study provides a method for a new approach useful for recycling oil-bearing mud residue.

**ACKNOWLEDGEMENTS**

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