Synthesis of Monolithic Porous Carbon Aerogels from Sorghum Straw and Their Application in Rapid Oil Removal

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I. Introduction

With the ever increasing development of petrochemical industry and the ever growing demand of crude oil and petroleum products, oil spillage and chemical leakage accidents occur frequently world-wide during exploration and transportation.1−6 Water pollution arising from these accidents is the most direct and severe consequence, which leads to shocking damage to the environment and the biosphere.7−13 Thus, it is urgent to develop suitable strategies for the rapid removal of oil from water. Typically, there are three methods successfully applied for oil spillage cleaning: chemical methods, bioremediation and physical adsorption.4, 6, 10, 13, 14 However, chemical treatments including in situ burning and solidification are costly and complicated.8, 15 Bioremediation using microorganisms to degrade toxic organic solvents is time-consuming and strongly influenced by the treatment condition.10, 16 Among so many strategies, the physical adsorption method is considered as the most fast and convenient way due to its low cost, simple operation and effectiveness.1, 7−9, 15

There have been several materials used for adsorbents for oil clean-up, such as polymers, natural materials, inorganic minerals, etc. Polymers like polypropylene and polyurethane possess good adsorption capacity, but they are difficult to degrade.5, 17, 18 Natural materials such as cotton, wool, straw, etc, are environmentally friendly, but they show poor adsorption ability and also absorb water at the same time.2, 4, 6 Therefore, materials with excellent adsorption ability and good hydrophobicity are urgently desired. Carbonaceous adsorbents with large porosity and hydrophobicity have attracted considerable attention in oil pollution treatment ascribed to their good chemical stability and environmental friendliness.8 Recently, activated carbons (ACs),2−3, 19, 20 porous carbon monoliths,21 carbon nanotube (CNT) sponges and their derivatives,3, 6, 7, 22, 23 graphene foams5, 6, 10, 24, 25 and cellulose-based carbon aerogels4, 4, 12, 18, 26, 27 were intensively investigated and have shown great application prospect in oil clean-up or oil-water separation. ACs exhibit good performance in the adsorption of organic solvents with small molecules, but they are limited in adsorbing heavy oil due to their numerous micropores excluding large oil molecules. Additionally, the ultrafine AC particles are difficult to be collected, which would introduce a secondary pollution.9, 19 Porous carbon monoliths facilitate the recyclability, however they are always fragile and dense in weight.2 CNTs or graphene sponges and their derivatives present excellent capacity in oil adsorption because of their ultralow density, high porosity, good hydrophobicity and superior flexibility. Nevertheless, the complicated synthetic procedure and the expensive raw materials have limited their practical applications.2, 24

Cellulose, the most abundant materials in nature, has recently gained lots of interests both academically and commercially due to their low cost, environment friendly, nontoxic and biodegradable properties.2−4, 8, 16, 27 For example, row cotton,2, 26 bamboo fibers,17 papers4 and bacterial cellulose28 have been employed to prepare 3D carbon framework for oil and organic solvents adsorption. They have shown superb capacity, even
better than CNT and graphene based aerogels. Despite of the outstanding adsorption ability, most of the biomass precursors for cellulose are not actually natural wastes. The utilization of biomass wastes as cellulose source is therefore of significant importance for the cost-effective generation of cellulose-based carbon adsorbents.

Herein, we reported an efficient synthesis of monolithic porous carbon aerogels from sorghum straws which are totally natural wastes and its application for oil rapid removal. In comparison with other sorbents, these MPCA materials showed excellent capacity and high stability in oil clean-up and good selectivity in oil–water separation.

2. Experimental section

2.1 Preparation

The shavings (1.0 g) peeled from sorghum straw were immersed in 70 mL KOH aqueous solution (3 mol L\(^{-1}\)) and then hydrothermally treated at 150 °C for 6 h. After cooling, the residue was homogeneously dispersed into 20 mL water under vigorously stirring. Then, the mixture was freeze-dried at −50 °C for 24 h. Followed by washing the solid to neutral and drying at 60 °C, the monolithic porous cellulose (MPC) was prepared. After carbonization in nitrogen atmosphere at different temperatures for 2 h, the MPCA absorbents were obtained. The finally obtained samples were denoted as MPCA-x (x = 4, 5 and 6, which corresponded to the carbonization temperature of 400 °C, 500 °C and 600 °C, respectively).

2.2 Structural characterization

Thermal stability of the MPC was characterized on a thermogravimetric analyzer (TGA4000 & STA6000, Perkin Elmer) with a heating rate of 10 °C min\(^{-1}\) from 35 °C to 800 °C in nitrogen atmosphere. The morphology of the samples was observed by scan electron microscope (SEM, FEI Quanta 250 FEG) which is equipped with an energy-dispersive X-ray spectrophotometer (EDS). Contact angles were measured by the Sessile drop method at room temperature and the ambient humidity with a Krüss (Hamburg, Germany) DSA-10 contact angle goniometer. Fourier transform infrared spectroscopy (FTIR) spectra of a sample in KBr pellet were recorded on a Nicolet Avatar 370 spectrometer. The Raman spectra of the samples were measured using an experimental apparatus consisting of a triple monochromator (TriVista TR557, Princeton Instruments) equipped with an argon ion laser (Coherent, CVI MELLES GRIOT) as a source of exciting light at 488 nm.

2.3 Oil adsorption tests of the MPCA

In a typical adsorption process, a piece of MPCA was weighted and immersed into a specific liquid for 20 seconds, and then taken out with tweezers. The sample was finely leaned on the edge of the liquid container to remove the excessive oil droplet before weight again. As for liquid with low boiling point, the measurement was done as quickly as possible in order to avoid the evaporation. The weight gain of the MPCA was calculated using the weight change of material before and after adsorption.

3. Results and discussion

As shown in Figure 1a, the sorghum straw before hydrothermal treatment did not present clear fibers in the field of vision which resulted from the lignin parts wrapping around the neighboring fibers to make them an integral whole. The sorghum straw was only composed of carbon and oxygen as seen in the EDS image (Figure 1b). Figure 1c showed the SEM image of the MPC, where a large amount of cellulose fibers with a length in millimeter scale and a diameter in tens of micrometers were found. These fibers in a high slenderness ratio are interconnected each other to form a 3D macroporous structure. In addition, an outstanding hydrophilicity was presented in the MPC because of the plentiful hydrophilic groups existing on the cellulose fiber surface. As illustrated in the inset of Figure 1c, the MPC could immediately suck up the water droplet as soon as it fell onto the surface. The TG curve of the MPC in N\(_2\) atmosphere was exhibited in Figure 1d. Three evident steps of weight loss were observed, which are respectively located in the range of room temperature−100 °C, 250−370 °C and 370−800 °C. The first stage, ~5 % weight loss, was related to the release of adsorbed water, and the ~60 % mass loss from 250 to 370 °C could be attributed to the discharge of abundant gases from the pyrolysis of cellulose. Finally, the further carbonization of skeleton contributed the ~20 % weight loss in the third step. The TG result suggested a carbonization temperature of higher than 370 °C was favorable. In this study, we employed 400, 500 and 600 °C to produce the MPCA to investigate the effect of the carbonization temperatures on the absorption capacity.
Figure 2 showed the digital photographs of the MPC and MPCA samples carbonized at various temperatures. A stable monolithic morphology of the MPC was obtained after the freeze-drying treatment. A low density of 22.0 mg mL$^{-1}$ was achieved in the MPC because of its developed porous structure. After the carbonization under inert atmosphere, the resulting MPCA samples (MPCA-4, MPCA-5 and MPCA-6) still retained the macroscopic shape of the MPC and no apparent decrease in their volumes was observed in comparison with the MPC. It indicated that the pyrolysis of cellulose at high temperatures did not destroy the porous structures of 3D interconnected fibers. What is more, the MPCA samples gained remarkable flexibility after carbonization. The MPCA-4 sample returned to its original, unloaded dimensions when the stress was released. However, the elasticity of the MPCA gradually declined as the carbonization temperature increased, and the MPCA-6 sample was highly crumbly.

The well preservation of the 3D porous structure in the MPCA samples was directly observed in their SEM images (Figure 3). As illustrated in Figure 3a, c and e, the spindling fiber morphology of the carbonized cellulose as well as the interfaced structure was similar to the pristine celluloses. The evaluated fiber diameters of the MPCA samples in the high-magnification SEM images (Figure 3b, d and f) was < 10 nm, which was smaller than that of cellulose fibers. It should result from the skeleton shrinkage after releasing volatile matters in the pyrolysis process. It was apparent that the conductivity of MPCA was improved with the enhancement of carbonization temperature based on the sharpness of their SEM images, indicating the increase of carbonization level. In addition, from the high-magnification SEM images, the surface of the fibers in MPCA-6 was very rough, different from the smooth surface of MPCA-4 and MPCA-5. It might be the reason for the poor mechanical property of MPCA-6. The examination results of
water contact degree were presented in the insets of Figure 3a, c and e. A significant hydrophobicity was revealed and the water contact degrees were 135.4°, 136.9° and 145.1° for MPC-4, MPCA-5 and MPCA-6, respectively.

The difference in the carbonization level for various samples could also be proved by the FTIR and Raman spectra. As shown in Figure 4a, the absorption bands at 3132 cm\(^{-1}\), 1620 cm\(^{-1}\) and 1072 cm\(^{-1}\) were respectively ascribed to the stretching vibrations of O–H, C=O and C–O groups. The intensity of these absorption bands gradually decreased as the temperature increased, demonstrating the decrease of the hydrophilic groups and the enhancement of the carbonization level from MPC to MPCA-6. In the wavenumber range of 2000–1000 cm\(^{-1}\) no signal appeared in the Raman spectrum of MPC (Figure 4b). With the high temperature carbonization, two pronounced peaks were found in the MPCA samples. The peak at about 1596 cm\(^{-1}\) corresponded to the G band denoting the ordered graphite lattice of carbon material and another at approximate 1356 cm\(^{-1}\) resulted from the D band that suggested the presence of disordered carbon structure. As the heating temperature increased, the intensity of D and G bands was enhanced from MPCA-4 to MPCA-6. It was another powerful evidence of the improvement of the carbonization level.

Figure 5a compared the adsorption capacities of the obtained MPCA materials towards various oily organic matters. All the adsorbents exhibited superior adsorption performance, and high adsorption capacities of 42–124 times of their own weight which were achieved from n-hexane, petroleum ether, toluene, phenixin, soybean oil, diesel oil and machine oil. Among them, the MPCA-4 sample possessed the better oil adsorption ability. By comparison with various adsorbents in the literatures (Table 1), the adsorption ability of MPCA-4 was comparable or even superior to those of the reported carbon-based adsorbents. The density of MPCA-4 was ~9.3 mg cm\(^{-3}\) which belongs to the range of ultra-low density material.\(^1\) As a result, it could even stand on the stamen of camellia sasanqua flower (Figure 5b) and float on the water surface (Figure 5c). Once it was contacted to the dyed toluene on the water surface, the toluene droplet was quickly adsorbed (Figure 5d). Furthermore, MPCA-4 also had an excellent adsorption behavior for the oily organic matters under water. As seen in Figure 5e, phenixin with high density presented on the bottom of vessel was immediately sucked up by the hydrophobic MPCA-4 which was forced to be immersed into water.

The superb mechanical property of MPCA-4 was demonstrated in Figure 6a. The deformed sample compressed by a 100 g counter weight could immediately recover as soon as removing the external force. Such magnificient flexibility provided an opportunity to recycle the used adsorbent by squeezing the oily organic matters out (Figure 6b). We estimated the reusability of MPCA-4 by adsorption/desorption of oil with two approaches; distillation and squeezing. Petroleum ether was used as model oil with low BP, which was completely released by distillation (Figure 6c). The recycled adsorbent could be reused and the adsorption capacity was well preserved in the
followed cycles. As for the high BP diesel oil that was not able to be desorbed by distillation, we discharged it by mechanical squeezing the used adsorbent. As shown in Figure 6d, most of the adsorbed diesel oil could be squeezed out in successive six cycles. Nevertheless, the adsorption capacity of the followed runs was slightly decreased in comparison with the first run. It should be ascribed to the twist of the carbon fibers under violent compression, therefore diminishing the pore volume unavoidably. After the first cycle, the adsorption performance became stable, which implied the splendid mechanical property of MPCA and the hydrophobicity was not destroyed by the mechanical squeezing.

4. Conclusions

We developed an ultralight MPCA material with the superior mechanical property, the outstanding hydrophobicity and the macroporous structure by using the agricultural waste of sorghum straw as the precursor. This inexpensive adsorbent has high adsorption capacity for various oily organic matters and could quickly adsorb the floated oil or sunk oil in water. Furthermore, the MPCA adsorbent could be recovered by releasing the adsorbed oil via distillation or mechanical squeezing depending on the boiling point of the oil. Such a cost-effective adsorbent with structural advantages and outstanding adsorption performance for oily compounds is promising for practical application in oil removal from water.

Acknowledgements

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Table 1. The comparison of adsorption ability of MPCA-4 with various adsorbents in the literatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Density (mg cm$^{-3}$)</th>
<th>Adsorbate</th>
<th>Sorption capacity (g g$^{-1}$)</th>
<th>Cost</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Graphene/polypyrrole foam</td>
<td>7−10</td>
<td>Toluene</td>
<td>36.8</td>
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<td></td>
<td></td>
<td>Diesel oil</td>
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<td>Graphene oxide-coated sponge</td>
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<td>10</td>
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<td></td>
<td></td>
<td>Olive oil</td>
<td>97</td>
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<tr>
<td>Graphene foam</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Diesel oil</td>
<td>24</td>
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<td>11</td>
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<td></td>
<td></td>
<td>Olive oil</td>
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<td>Polydimethylsiloxane-coated cotton</td>
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<td>Toluene</td>
<td>26</td>
<td>medium</td>
<td>26</td>
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<td></td>
<td></td>
<td>Diesel oil</td>
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<td>Macro/mesoporous carbon monoliths</td>
<td>15−19</td>
<td>Toluene</td>
<td>27</td>
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<td>21</td>
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<td>Soybean oil</td>
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<td>Bamboo fibers</td>
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<td>Diesel oil</td>
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<td></td>
<td></td>
<td>Colza oil</td>
<td>105</td>
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<tr>
<td>MPCA-4</td>
<td>9.3</td>
<td>Hexane</td>
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<td>quite low</td>
<td>present work</td>
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<tr>
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<td>Toluene</td>
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<td></td>
<td>Soybean oil</td>
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Figure 6. (a) Photographs of the experiment of MPCA-4 compressed by a 100 g counter weight; (b) Photographs of the recycling of adsorbed toluene dyed by Sudan I via the mechanical squeezing; The distillation recyclability of petroleum ether (c) and the squeezing recyclability of diesel oil (d).
Research Article

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