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Production and Characterization of Carbonaceous Adsorbents from Biomass Wastes by Aqueous Phase Carbonization

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Abstract. This paper deals with a method to produce carbonaceous adsorbents from biomass using a technique of aqueous phase carbonization (hydrothermal carbonization). A series of laboratory-scale tests to produce carbonaceous materials from existing biomass such as Japanese cedar, which is a typical construction material in Japan, were conducted. The biomass feedstock was subjected to (1) hydrothermal carbonization at 350°C, followed by (2) hydrothermal oxidation at 350°C with the existence of hydrogen peroxide and (3) short-tome heat treatment at 950°C in a closed crucible with no water. Thus-obtained carbonaceous materials were found to have mesoporous structures with ca. 350 m^2/g of specific surface area and the adsorption capacity for phenol could reach to around three-quarters of that of a commercial activated carbon.

Keywords: adsorption, biomass, mesoporous adsorbent

1. Introduction

Carbonaceous adsorbents, such as activated carbon, are among the most popular adsorbents and are widely used in various types of adsorption processes. Generally, the production process of carbonaceous adsorbent involves pyrolysis of the raw feedstock to create an intermediate carbonized material, followed by the activation step to grow its porous structure. The intermediate carbonized material is usually made from biomass (e.g., nut shells) or fossil source (e.g., coal), processed at a high temperature under a dry condition. Recently, a technique to carbonize biomass in pressurized hot liquid water has been developed (Inoue et al., 2002; Sato et al., 2004). The aqueous phase carbonization process is a promising method to produce carbonaceous materials from some biomass feedstock having high moisture contents, because it does not require a drying process in which much energy is consumed. We have developed noncatalytic hydrothermal treatment to obtain useful chemicals from biomass, such as rice husks, spent molt and wood (Mochidzuki et al., 2000, 2001, 2003). The process generates a cretin amount of moist biomass residues, which is partly carbonized, as well as the target chemical products. We focused on the carbonization of such moist residues in pressurized hot liquid water at moderate temperatures (<350°C). On the other hand, a method to oxidize carbon in pressurized hot liquid water, which can provide an alternative to the conventional activation manner by steam or carbon dioxide treatment at higher temperatures, has been reported (Tam et al., 2001). Using some nut shell charcoals, activated carbons having specific surface areas of 500–1000 m^2/g, were obtained in the aqueous method with less energy consumptions at remarkably high yields.

In the present study, we investigated a method combining the above findings to produce activated carbons from biomass feedstock. That is to say, both carbonization and activation were performed in aqueous phase. A series of laboratory-scale tests were conducted using an existing biomass feedstock; i.e., Japanese cedar, which is a typical construction material and great amount of its wastes are generated in Japan. The biomass was primary carbonized at 350°C with no oxidant, and then it was subjected to aqueous phase oxidation at the same

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temperature under the coexistence of hydrogen peroxide. Thus-obtained carbonaceous materials were characterized by measuring the porous properties, i.e., specific surface area and pore size distribution. To evaluate the adsorption capacities, the adsorption equatorial for phenol in aqueous phase were also examined.

2. Experimental

Figure 1 shows the experimental procedure for the hydrothermal treatment to obtain carbonaceous materials (samples #1–#6). As the biomass feedstock, *SUGI* (Japanese cedar, *Cryptomeria*) grown in Chiba, Japan was used. The feedstock was ground into powder (180–425 μm) prior to the experiment. For the comparison, a commercial charcoal made from *NARA* (Japanese oak, *Quercus serrata*) was subjected to 10% hydrogen peroxide treatment (sample #7) followed by heat treatment (#8).

The biomass feedstock (Japanese cedar) and deionized water were put into a pressure vessel (Hastelloy C-22, volume = 66 ml) at a ratio of 3 g: 30 ml. Sealed it tightly, the vessel was heated in a salt bath at 350°C for 60 minutes (Fig. 2). After the treatment, the vessel was cooled down in a water bath and then the product (hydrothermal charcoal) was collected. The secondary carbonization/oxidation of the hydrothermal charcoal was performed in the same manner using 3% or 10% hydrogen peroxide in place of water at a ratio of 1 g: 30 ml. Finally, the sample oxidized by hydrogen peroxide (oxidized hydrothermal charcoal) was treated in a closed crucible within a muffle furnace with no water at 950°C to remove remaining volatile matter. Thus obtained carbonaceous sample (burnt, oxidized hydrothermal charcoal) was provided to the following tests: i.e., BET surface area and pore size distribution by nitrogen adsorption (BEL SORP MINI, BEL Japan) and CHN ratio (2400-II, Perkin Elmer). To evaluate the adsorption capacities of the carbonaceous materials obtained, the adsorption isotherms for phenol were measured in a series of batch system adsorption tests at 25°C.

3. Results and Discussion

The experimental results; i.e., yields and BET specific surface areas (BET-SA), for the Japanese cedar and the commercial charcoal are summarized in Table 1. By the primary hydrothermal carbonization, the Japanese cedar sample was converted into charcoal (hydrothermal charcoal, sample #1); however, this sample had only 5.3 m^2/g of BET-SA. Incidentally, the yield of carbon in this step was only 14.0; nevertheless, some chemicals, e.g., furfurals and organic acids, could be obtained from the aqueous solution. The short-time heat treatment at 950°C in the muffle furnace enhanced its surface area and the value of BET-SA was found to be 231 m^2/g (burnt hydrothermal charcoal, sample #6). During the hydrothermal carbonization process, not only carbonization but also solubilization of the organics and formation of the tarry substances occurred. The hydrothermal charcoal, sample #1, could be contaminated with such substances and these contaminants

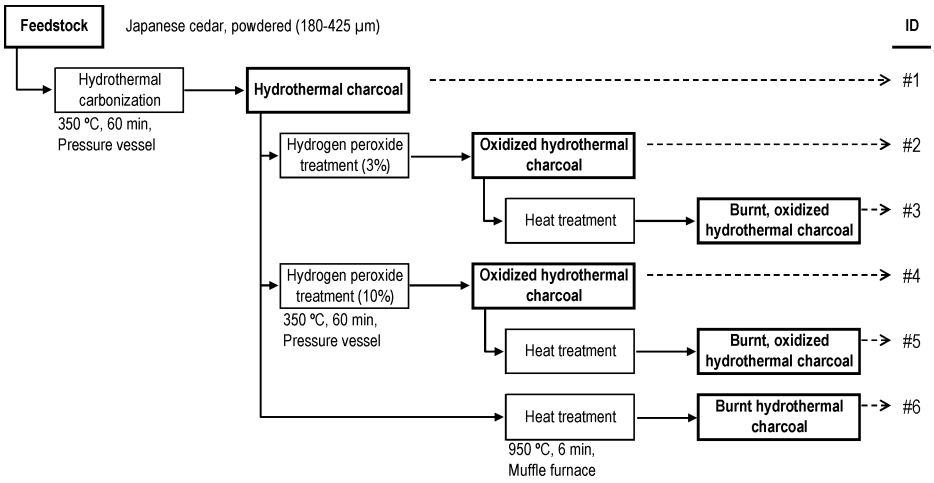

Figure 1. Procedure for the hydrothermal carbonization to obtain carbonaceous materials.

Table 1. Summary of the experimental results.

Sample ID	Yield (1) [%]	Yield (2) [%]	BET-SA (m^2/g)
Japanese cedar			
#1: hydrothermal charcoal	14.0	—	5.3
#2: oxidized hydrothermal charcoal (3% H_2O_2)	84.6	11.8	77.4
#3: burnt, oxidized hydrothermal charcoal (3% H_2O_2)	69.3	8.2	325
#4: oxidized hydrothermal charcoal (10% H_2O_2)	67.4	9.4	223
#5: burnt, oxidized hydrothermal charcoal (10% H_2O_2)	67.7	6.4	335
#6: burnt hydrothermal charcoal	66.7	9.3	231
Commercial charcoal			
#7: oxidized charcoal (10% H_2O_2)	86.0	—	324
#8: burnt, oxidized charcoal (10% H_2O_2)	90.3	77.7	352

Yield (1): at each step, yield (2): against feedstock.

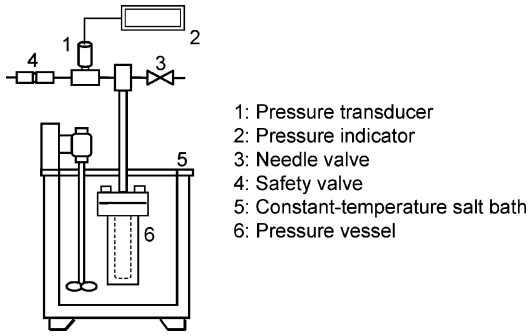

Figure 2. Schematic diagram of the experimental set-up for hydrothermal carbonization.

plugged the pores. Because of this, the apparent BET-SA of sample #1 showed a very small value. In fact, washing it with acetone extracted lots of tarry stuff. Treated at 950°C, the contaminants were removed and the pore structure appeared to result the higher surface area. The C/H ratio was remarkably increased from 19 (sample #1) to 136 (sample #6) during the heat treatment. On the other hand, the secondary treatment with hydrogen peroxide also increased BET-SA (oxidized hydrothermal charcoals, samples #2 and #4). The reaction with the oxidant decomposed the remaining tarry substances and might oxidize the surface of the carbon to develop the porous structure. When using 10% hydrogen peroxide (sample #4), its BET-SA was almost the same as that of sample #6 which was treated at 950°C in the muffle furnace. The C/H ratios of samples #2 and #4 were 21 and 24, respectively. Compared them with that of the hydrothermal charcoal (C/H = 19), the values for the C/H ratio of these three samples were in the same magnitude. This suggested that the secondary treatment under the coexistence of the oxidants could not achieve complete carbonization and the surface functional groups remained and/or increased, while the short-time heat treatment at 950°C produced highly carbonized charcoal. When the oxidized hydrothermal charcoals were subjected to the short-time heat treatment at 950°C, completely carbonized charcoals with higher BET-SA were obtained (burnt, oxidized hydrothermal charcoals, samples #3 and #5). Their C/H ratios were found to be 161 and 201, respectively. The values of BET-SA of these samples (325 and 335 m^2/g, respectively) were as large as one-third of that of typical commercial activated carbons. While the difference in the BET-SA between samples #2 and #4 (oxidized hydrothermal charcoals) was quite large, that between samples #3 and #5 (burnt, oxidized hydrothermal charcoals) was slight. This suggested that the treatment with 3% hydrogen peroxide was insufficient to decompose/remove the tarry contaminants, but it created "seeds" of the pores to provide lager surface area. In fact, as can be seen from yield (1), the amount of the substances decomposed/removed in the 3% hydrogen peroxide treatment was relatively small. The weight loss during the 3% hydrogen peroxide treatment was only 15.4%, while that during 10% hydrogen peroxide treatment was 32.6%.

For a comparison, a commercial charcoal was treated in the aqueous phase in the same manner. The BET-SA of the untreated charcoal was 263 m^2/g, and it was increased to 324 m^2/g by the 10% hydrogen peroxide treatment in pressurized aqueous phase at 350°C. By the following short-time heat treatment, the increase

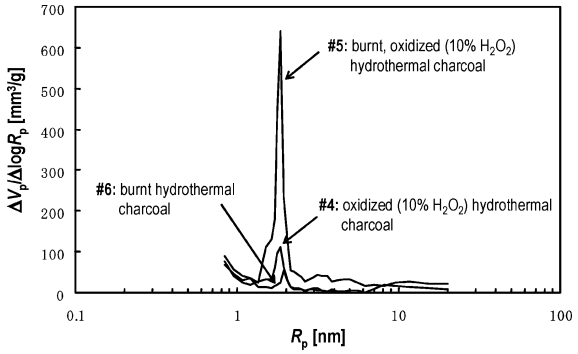

Figure 3. Pore size distributions for the carbonaceous materials obtained from Japanese cedar.

in the surface area was not obvious. In addition, the changes in the weight during those steps were not so much.

Figure 3 shows the pore size distributions for the samples #4, #5 and #6. It can be clearly seen that a mesoporous material with the pores having R_p around 2 nm was produced thorough the series of treatment. Incidentally, the pore volume around $R_p = 2$ nm of the burnt, oxidized hydrothermal charcoal (sample #5) was larger than that of a commercial activated carbon, although its BET-SA was much smaller. On the other hand, it was impossible to observe mesoporous in the measurements for the materials produced from the commercial charcoal. In general, charcoals which carbonized at higher temperatures have very small pores (micropores/sub-micropores) because of the shrinkage; however, the hydrothermal charcoal might not shrink so much during the carbonization step in aqueous phase at a moderate temperature. The commercial charcoal used in this study did not have mesopores originally. The hydrothermal treatment under the coexistence of hydrogen peroxide did not create mesopores on such a charcoal. In our previous work (Li et al., 2001) it was found that supercritical water oxidation of carbon fibers did not create pores on the surface of the carbon fibers, neither. It was suggested that the aqueous phase oxidation was not so strong, compared with the ordinal activation techniques used in the industrial activated carbon production processes. The base of the mesoporous structures of the hydrothermal charcoals were formed during the primary carbonization step. The post-treatments; i.e., the hydrogen peroxide treatment and short-time heat treatment, were supposed to clean up the carbon surfaces and enlarge the pores.

To evaluate the adsorption capacities of the obtained carbonaceous materials, the adsorption isotherms for phenol in aqueous solution were measured at 25°C, and compared with a commercial coal-base activated carbon for water treatment. As shown in Fig. 4, the burnt, oxidized hydrothermal charcoal (sample #5) were found to adsorb a considerable amount of phenol, and the adsorption capacity was as high as about three-quarters of that of the commercial activated carbon. On the other hand, the burnt, oxidized charcoal (sample #8) showed much lower adsorption capacity than sample #5, though their surface areas were similar to each other. Needless to say, the amount adsorbed depends upon not only the surface area but also the pore size distribution. The mesoporous structure of the carbonaceous material obtained in this work matched the molecular size of phenol. It should be a promising adsorbent to remove cyclic or poly-cyclic compounds. For example, Nagano, Tamon and their coworkers suggested that mesoporous activated carbons were necessary for adsorption of dioxins (Nagano et al., 2000). Further exploitation of the application of the mesoporous carbonaceous material is undergoing.

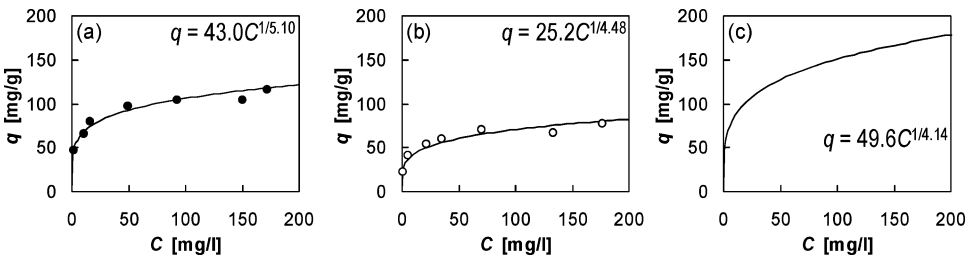

Figure 4. Adsorption isotherms for phenol, (a) burnt, oxidized hydrothermal charcoal (sample #5), (b) burnt, oxidized charcoal (sample #8), and (c) commercial coal-base activated carbon (BET-SA = 1050–1200 m^2/g in specification)

4. Conclusions

A mesoporous carbonaceous adsorbent was successfully produced in the aqueous phase carbonization followed by some post-treatments. The carbonization and activation steps could be expressed as follows: (1) the biomass was carbonized and pores grew but the pores were plugged by the tarry staff in the primary carbonation, (2) the secondary treatment with hydrogen peroxide decomposed/removed a part of the tarry stuff and oxidized the surface of the carbon to develop the porous structure and increase surface functional group, and (3) the remaining tarry stuff and the surface functional groups were removed by heating in the closed crucible at 950°C. This-obtained carbonaceous material had a mesoporous structure and had an adsorption capacity that can be comparable to a commercial activated carbon for water treatment.

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