Spent coffee ground based adsorbent synthesis by hydrothermal carbonization

（水熱炭化によるコーヒー滓からの吸着剤合成）

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1. Introduction

According to the coffee consumption data from International Coffee Organization (ICO), it can be speculated that in 2018, about 6.5 million tons of spent coffee grounds (SCG) were generated, the amount of which is over 2 times of SCG generated in 1990 [1]. However, landfill is still utilized as the main SCG treatment method due to its low cost and convenient operation, which leads to emission of greenhouse gases and ground water contamination concerns. On the other hand, as the roasted coffee beans originated SCG has already underwent preparatory carbonization to some extent, it is an ideal material to be tailored into functional carbonaceous materials.

Hydrothermal carbonization (HTC) is an attractive thermochemical synthesis alternative to produce functional carbon materials from SCG. This process is energetically favorable when compared to traditional pyrolysis, because it uses milder conditions, does not need drying of the feedstocks and is exothermic. The solid product synthesized by HTC is referred to as hydrochar. Hydrochar comprises condensed aromatic structures and bears high concentrations of oxygenated functional groups (OFGs). These properties offer the advantage of further functionalization and make hydrochar more hydrophilic for suitable applications of adsorption and as a precursor for activated carbon synthesis. [2]

Lignocellulosic biomass derived hydrochar is a good adsorbent material for heavy metal adsorption in wastewater treatment because its high content of surface OFGs enhance its adsorption selectivity, ion change capacity and metal affinity. Meanwhile, it can also be prepared as a good precursor for the synthesis of porous activated carbon via chemical activation because the high chemical reactivity of hydrochar improves its porosity development in activation. [3] Thus, HTC process conditions can be tuned to prepare hydrochar for achieving good activation. The aim of this study is to investigate how HTC operating conditions affect the activation extent of SCG hydrochar derived activated carbon and to make a clarification of the possible reason through observing the physicochemical properties of hydrochar precursors and hydrochar derived activated carbons. Finally, zinc adsorption experiments were conducted to evaluate the performance of SCG hydrochar and SCG hydrochar derived activated carbon in practical applications.

2. Experimental

Hydrothermal carbonization: a batch-type reactor made of stainless steel (SUS 316) with inner volume of 29.3 mL was used in this study. The starting material, mixture of dry SCG obtained from student cafeteria in Kashiwa Campus and deionized water, was prepared in mass ratio of 1:2 (4 g SCG and 8 mL water or 8 mL 5% HNO_3 solution for acid modification) or 1:5 (1 g SCG and 5 mL water). HTC reactions were initiated by immersing the reactor into the molten salt bath in the temperature range from 180℃ to 300℃. After predefined time (2 h or 4 h), the reactor was quenched to stop the reaction. The solid product, or hydrochar, obtained from the reactors was separated by vacuum filtration followed by drying in an oven at 105℃ overnight.

Chemical activation: the former synthesized hydrochar was mixed with KOH in the ratio of 1:3

(2 g dry SCG hydrochar and 6 g KOH powder) and then heated to 600℃ in a tube furnace under nitrogen gas protection for 1 h. After that, open furnace cover to let the temperature cool down soon to stop the activation reaction. The activated samples were taken out and then thoroughly washed several times with 10% HCl to remove any inorganic salts, and further washed with distilled water until neutral pH. Finally, the activated carbon was dried in an oven at 105℃ overnight.

Water treatment test: the zinc adsorption test was performed by a magnetic stirrer. 50 mg of activated carbon sample was added into 100 mL $Zn(NO_3)_2$ solution in a 200 mL beaker and agitated until equilibrium in 8 hours at 27℃. For one type of activated carbon sample, serval adsorption tests were performed with different zinc ion concentration (10, 25, 50, 60, 80, 100, 200 ppm) at the same temperature (27℃) and pH value (5). The concentration of zinc solution after equilibrium was determined by ICP-MS. Finally, Langmuir's isotherm was fitted to obtain the adsorption capacity of each sample in zinc adsorption.

3. Results and discussion

3.1 Synthesis of SCG hydrochar

SCG hydrochar samples were synthesized under SCG/water ratio of 1:5 and reaction time of 2 h. Proximate analysis results and mass yield of samples named as (m)x-HC (x represents the operating temperature of HTC, m represents 5% HNO_3 modification and HC stands for hydrochar) are presented in Figure 1. With increasing HTC temperature, the sample was carbonized further and the mass yield got lower, and the HNO_3 additive in HTC process obviously increased the carbonization extent.

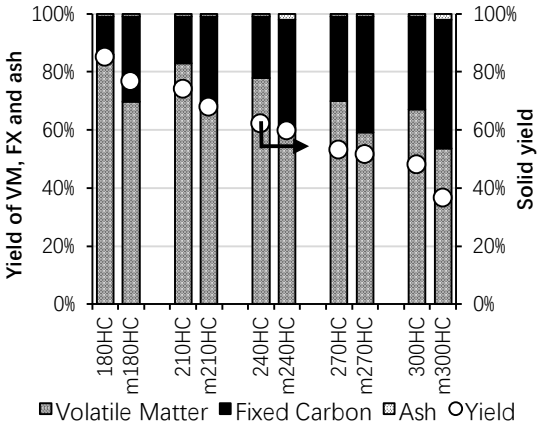

Figure. 1. Proximate analysis and mass yield of hydrochar

The SEM image of (a) raw SCG material, (b)SCG hydrochar synthesized by HTC at 240℃, (c) SCG hydrochar synthesized by HNO_3 assisted HTC at 240℃ are shown in Figure 2. Figure 2b revealed that the particles retain the appearance of the raw material as shown in Figure 2a. The spheres observed as marked by the arrow, are assumed as the carbon microspheres derived from cellulosic fraction. From Figure 2c, we can see addition of HNO_3 promoted the hydrolysis of the organic substrate and facilitated the dehydration of decomposed soluble matter to form carbon microspheres in HTC process. These results explained why fixed carbon content was higher with hydrochar prepared under HNO_3 assisted HTC.

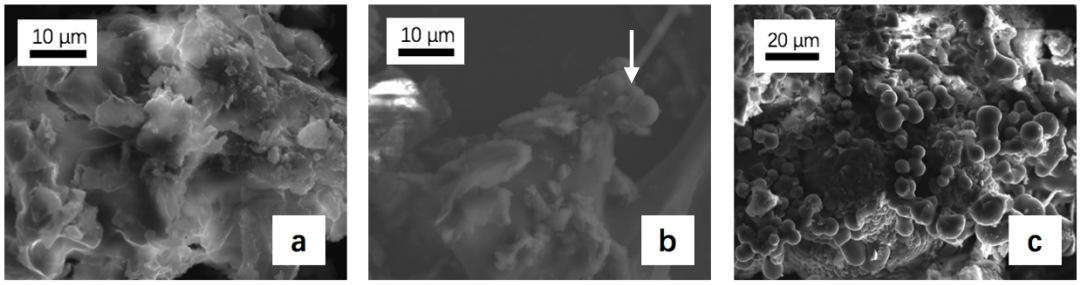

Figure. 2. SEM image of raw SCG, hydrochar obtained after 240℃ HTC and 240℃ HNO_3 assisted HTC

As illustrated in Figure 3, these hydrothermal carbon particles consist of small clusters of condensed benzene rings that form stable groups with oxygen in the core, whereas the shell possesses more reactive/hydrophilic oxygen functionalities. [4] This kind of structure with reactive surface increases the ion exchange capacity and the metal affinity, which is in favor of heavy metal removal in wastewater treatment.

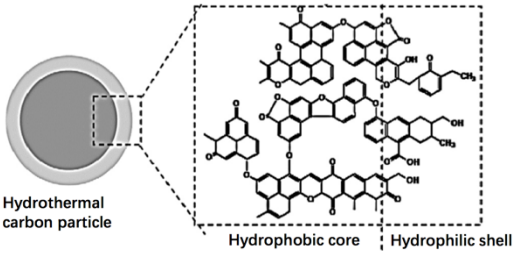

Figure. 3. Structure of hydrochar carbon particle [4]

Figure 4 shows the zinc adsorption amount of hydrochar synthesized under different HTC temperature. Hydrochar synthesized at 240 ℃ performed better than other hydrochar. It was considered that more OFGs, especially the carboxyl groups and hydroxyl groups, could offer more exchangeable H^+ ion to adsorb zinc ion by electrostatic interaction. [5] Thus, at a lower HTC temperature, cellulosic matters were too stable to be decomposed, so the content of OFGs content was low. In contrast, the condensation of hydrochar and decomposition of OFGs will likely to take place excessively as higher HTC temperature.

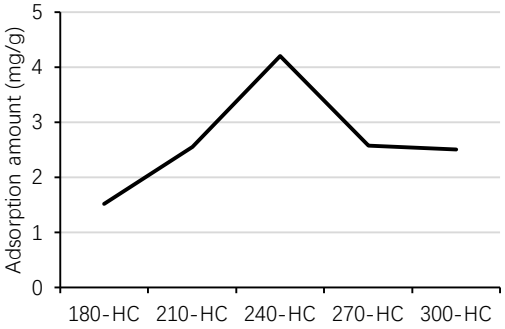

Figure. 4. Zinc adsorption amount of SCG hydrochar samples

3.2 Synthesis of SCG hydrochar derived activated carbon

The SEM image of activated carbon synthesized through KOH chemical activation derived from 240-HC (a) and m240-HC (b) are shown in Figure 5. The activated carbons exhibit irregular shaped particles with large cavities, which indicates that a drastic morphological transformation took place during the chemical activation process.

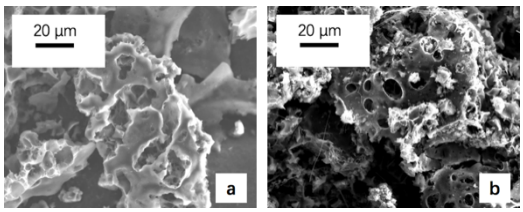

Figure. 5. SEM images of activated carbon derived from 240-HC (a) and m240HC (b)

The N_2 adsorption and desorption isotherms and pore size distribution of activated carbons are shown in Figure 6 (AC in their name means they are activated from corresponding hydrochar). Figure 6a reveals that 240-AC has the largest N_2 uptake, arising from a higher porosity development

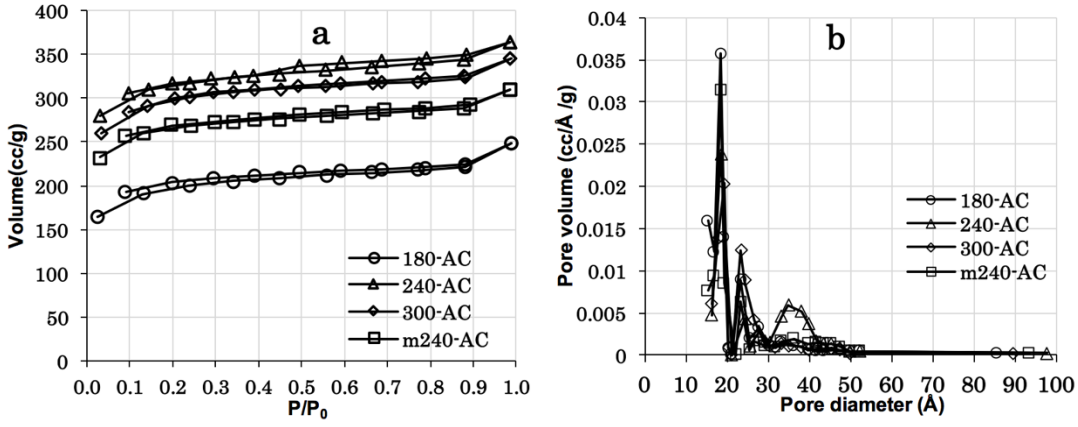

Figure. 6. (a) N_2 adsorption and desorption isotherms and (b) pore size distribution of hydrochar derived activated carbon

than other activated carbons. This hypothesis was also supported from the highest specific surface area and total pore volume values (results not shown in this abstract). In addition, 240-AC sample presents broader pore size distribution especially larger mesopore area than other activated carbons as shown in Figure 6b. It could be explained that during KOH activation, H^+ ion in carboxyl groups and hydroxyl groups is easily exchanged by K^+, which affects the electron cloud distribution of aromatic carbon, increases the active point of carbon material and makes the material easier to be activated. [6] Therefore, high OFGs content is in favor of high porosity development. While in the case of m240-AC, it can be speculated that extensive dehydration happened in HNO_3 assisted HTC and that the product hydrochar underwent excessive chemical reaction during activation, which destructed its pore structure.

The results of mass yield and zinc adsorption capacity of hydrochar derived activated carbons are shown in Figure 7. We can see that activated carbon from HTC temperature at 240℃ (240-AC) showed the highest zinc adsorption capacity among all samples. Meanwhile, HNO_3 assisted HTC process resulted in decrease of zinc adsorption capacity at all HTC temperatures. This is because most of zinc ion exists in low pH solution (in this experiment, pH=5) are in the form of hydrated zinc ion clusters like $[Zn(H_2O)_6]^{2+}$. These ion clusters are in large size so that they can enter mesopores of activated carbon more easily rather than micropores of activated carbon. From Figure 6b, we can see m240-AC didn't show large pore volume in mesopore areas when compared to 240-AC.

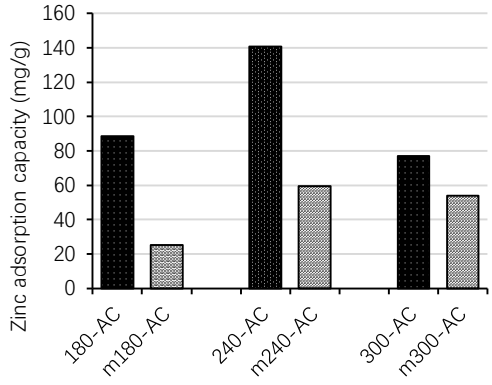

Figure. 7. Zinc adsorption capacity of activated carbons

4. Conclusion

HTC is a simple, promising conversion technique of converting waste SCG to value-added products. SCG hydrochar utilized as carbonaceous adsorbent and precursor of porous activated carbon was successfully synthesized by HTC in this study. It was found that hydrothermal treatment operating conditions greatly affected the chemical properties of this kind of SCG hydrochar as well as activated carbon derived from it, thus affected the practical application performance like zinc adsorption in water treatment. In the hydrothermal operating condition under SCG/water ratio of 1:5 and reaction time of 2 h, it was found that 240 ℃ is the most suitable reaction temperature to produce high performance hydrochar adsorbent as well as best precursor for porous activated carbon synthesis. Meanwhile, activated carbon derived from hydrochar prepared by 5% HNO_3 assist HTC process didn't show progress in pore development.

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