Preparation of Lotus Root-Type Monolithic-Activated Carbons with an Hierarchical Pore Structure from Rice Husks and Their Adsorption of Vitamin B12

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ABSTRACT: Activated carbon is widely used in many fields because of its well-developed pore structure. Especially in hemoperfusion, activated carbon beads derived from macroporous resin spheres are the predominant adsorbents in hemoditoxifiers. In comparison, biomass-activated carbon attracts more extensive attention on account of its renewability and environmental protection. In this study, a lotus root-type monolithic-activated carbon with a hierarchical pore structure was made from rice husks by the injection molding process followed by carbonization and activation. The straight square channels with the side length of about 1.3 mm were designable, and these channels with adjustable lengths were favorable for the fluid flow during blood purification compared with the tightly packed carbon beads in commercialized hemoditoxifiers. Complementally, the hierarchical nano-sized pores in the walls of the big channels would contribute much to the adsorption capacity for the monolith. Specifically, the adsorption of vitamin B12, a representative of middle molecular toxins in human blood, was about 3.7 mg g\(^{-1}\), which was acquired by simulated in vitro hemoperfusion tests and this demonstrated the promising application of the lotus root-type biomass-activated carbon in hemoperfusion.

INTRODUCTION

Activated carbon (AC) has attracted various applications such as energy storage, catalyst, adsorption, and medical facility (hemoditoxifier) because of its light weight, hierarchical pore structure, and other unique properties. The raw materials of AC derive from a wealth of sources, including coal tar pitch, sludge, ore, sawdust, and biomass materials. By contrast, preparation of AC from renewable biomass materials has been focused widely all the time because they are cheap, renewable, and environment friendly with extensive sources. For example, the coconut shell is a well-known precursor for the production of high-quality granular AC, which has been applied as electrode materials in supercapacitors and adsorbents for textile dyes. Similarly, Gercel et al. took AC, which was made from Euphorbia rigida, to remove dispersed dye from aqueous solution, and the maximum adsorption capacity of Disperse Orange 25 was 118.93 mg g\(^{-1}\) at 20 °C. Aytun et al. prepared granulated AC from several biomass materials (almond shells, hazelnut shells, walnut shells and apricot stones) and investigated their adsorption for phenol and methylene. Particularly, for Pb (II) and Cu (II) in wastewater, powdery AC derived from cassava peels was proved to be an efficient adsorbent on account of its well-developed microspores (0.14 cc g\(^{-1}\)) and high specific surface area (473 m\(^2\) g\(^{-1}\)). In comparison, rice husks are another abundant biomass raw materials for the production of AC. Because of the high ash content (20%), most of which is silica, rice husks are easy to be activated into porous materials by activators like lye solution, zinc chloride, or just water steam. Tannin studied water purification by rice husk-derived AC as early as in 1989, and then it was also explored to be used as current collectors.  

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and adsorbents for various dyes and some organic pollutants like Rhodamine B and phenol.

Generally, AC derived from biomass raw materials is powdery or irregularly granulated and it cannot be used directly in some fields such as hemoperfusion because the dissociative powders may cause secondary "pollution", and the sharp edges of as-prepared irregular-shaped particles may cause damage to some hemocytes in human blood. Therefore, in hemoperfusion, spherical AC particles were developed as the adsorbent to clear away uremia toxins including middle molecules (e.g., leptin, peptides) and protein-bound molecules (e.g., p-Cresol, indoxyl sulfate), in which hemodialysis could not solved. However, the flow resistance of blood through the densely packed AC beads is nonnegligible, and concomitantly, the chances of the collision between the blood cells and the beads during the blood flowing through in the tortuous passageway would increase dramatically. To avoid this problem, AC could be prepared in monolith with hierarchical pores to lower pressure drop and promote adsorption capacity. For example, Yu at al. obtained honeycomb briquette-shaped activated charcoal with $2 \text{ mm} \times 2 \text{ mm}$ square channels by directly extruding AC paste and then took it to adsorb volatile organic compounds. Bai et al. prepared hierarchically porous cellulose/AC composite monoliths to remove toxic dyes from waste water.

In this study, rice husks, which used to be the precursor for producing powdery AC, were taken as the main raw material to produce lotus root-type monolithic AC with hierarchical pores by an injection molding process, followed by carbonization and activation. The morphology, microstructure, and chemical composition were characterized, and especially, the pore structure evolution was studied before and after carbonization and activation by nitrogen adsorption analyses and mercury intrusion tests. Particularly, the adsorption of vitamin B12 (VB12), a representative of middle molecular toxins in human blood, was evaluated by a self-designed testing platform which simulated the in vitro hemoperfusion process.

## RESULTS AND DISCUSSION

**Morphology, Microstructure, and Chemical Composition.** The morphology and microstructure of the carbonized rice husks and the monoliths after being carbonized and activation are shown in Figure 1. The size of the grinded particles of carbonized rice husks was about several to dozens of micrometers, which was comparable to the size of powdery binder, that is, carboxy methyl cellulose (CMC). The monoliths were cylindrical with adjustable diameters and lengths. The intersection was uniformly distributed with lotus root-type square holes. The side length was about 1.3 mm, and the wall thickness was about 0.7 mm. After being activated, more big pores appeared in the cross-section of the pore walls (Figure 1c,d). Compared to densely packed spherical adsorbents in the commercialized hemodixifier, the lotus root-type monolithic AC could not only lower the pressure drop during hemoperfusion because of the straight long channels but also avoid the frequent harmful collisions between the hemocytes and the densely packed spherical adsorbents during their flow through the circuitous channels in practical hemoperfusion. Besides the millimeter-sized straight channels in the lotus root-type monolith, plentiful macro, meso, and micropores in the channel walls were crucial to adsorb the toxins in the solution or human blood. The detailed analyses about the pore structure would be discussed in the next section.

It is well known that not only the pore structure but also the chemical composition, especially the surface functional groups, would influence the adsorption properties of the adsorbent. In this study, Raman and infrared spectra were adopted to examine the chemical variations of the monolith after carbonization and activation. According to Raman results in Figure 2a, we could find that there was no big difference between the carbonized and activated samples, which indicated that the (002) planar crystal structure varied little. Similar low $I_D/I_G$ values in both carbonized and activated samples indicated that the carbon in the monoliths was mainly defective. Nevertheless, although the defects were detrimental to mechanical and electrical properties, they would conduce to activation, and moreover, the ubiquitous defects would be active sites, which were favorable for efficient adsorption. Furthermore, Fourier transform infrared (FTIR) results (Figure 2b) indicated that the chemical bonds experienced a huge change before and after carbonization. There were a large number of functional groups such as $-\text{OH}$ (3500–3400 cm$^{-1}$), $-\text{COOH}$ (3300–2500 cm$^{-1}$), and $\text{N-O}$ (1570 and 1553 cm$^{-1}$) in the carbonized samples. In addition, silicon (Si)-related chemical bonds such as $\text{Si-O}$ (1086 and 1080 cm$^{-1}$) and $\text{O-Si-O}$ (461 cm$^{-1}$) were discernible as well. However, after activation, most oxygen-related functional groups were disappeared, only a little $-\text{OH}$ and $\text{O-Si-O}$ remained. The analyses about the variation of chemical groups could be further corroborated by X-ray photoelectron spectroscopy (XPS) data (Figure 2c). The ratio of $\text{C/Si}$ increased from 9.50:1 to 12.33:1 after activation, and the atomic ratio of Si decreased to 5.91%. The decrease of oxygen was in accordance with the FTIR results in which $-\text{OH}$ and $-\text{COOH}$ were removed.

**Analyses of Pore Structures.** Detailed pore structures of the monoliths were investigated by N$_2$ adsorption–desorption isotherms (Figure 3a,b) and mercury intrusion method (Figure 3c). The adsorption isotherms of lotus root-type monolithic AC exhibited both the character of Type I, which was the typical adsorption isotherms of traditional AC and that of Type H4, which always indicated the existence of slit-like mesopores. More specifically, at ultra-low pressure ($p/p_0 < 0.01$), the adsorption volume increased a bit, which indicated that there were some micropores while the amount was limited. As the relative pressure increased ($0.01 < p/p_0 < 0.8$), the adsorption capacity increased rapidly and the desorption

**Figure 1.** SEM images of rice husk-derived powders after precarbonization (a,b). Also, SEM images of the monolith after carbonization (c) and activation (d).
Hysteresis loop of Type H4 appeared, which demonstrated the existence of narrow slit-like mesopores. At higher pressure (0.8 < p/p₀ < 1.0), there was no distinct growth about the pore volume. Based on the results from the quench solid density functional theory (QSDFT) method (inset of Figure 3b), we could find that before activation, the micropores were mainly in the range of 1.0−1.5 nm with a single peak at about 1.2 nm. After activation, the size distribution of micropores in the samples demonstrated a bimodal distribution, that is, one peak at about 1.0 nm and the other at about 1.5 nm. Moreover, a large number of mesopores with a peak diameter at about 2.2 nm was produced, and the volume of the initial mesopores with a peak diameter at about 5 nm was enlarged remarkably (Figure 3b). In addition, the results from mercury intrusion examinations showed that the sizes of macropores concentrated in the range of 1−3 μm (Figure 3c). Therefore, as a whole, the alkali activation process not only broadened the initial micropores but also created more micropores and mesopores in the channel walls. Specifically, the pore volume and specific area of the ultimate monolithic sample achieved 1.28 mL g⁻¹ and 329 m² g⁻¹, respectively. The volume of mesopores and micropores increased more than two times after activation treatment (Table 1). This indicated that alkali activation was rather efficient for rice husk-derived carbon, and this might be attributed to the inherent siliceous materials in
rice husks which was active to alkali. As a whole, the monolith derived from the biomass carbon with a hierarchical pore structure could be expected to be a promising adsorbent.

**Adsorption Capacity.** VB12 was usually adopted as the representative of middle molecular toxins in hemoperfusion tests.24 The molecular weight of VB12 was 1355 Da with the size of about 2.09 nm.4 Adsorption tests showed that the adsorption capacity of the powdery AC was 10.6 mg g\(^{-1}\). Obviously, it could not be used directly as the adsorbent in hemoditoxifiers because the probable secondary "pollution" for the tiny particles might pass through the filter screens at the two ends of the instrument and enter the bloodstream, although inevitably, the adsorption capacity would decrease once the AC particles were fabricated into an integrated monolith. Figure 4 shows the adsorption curves of the monoliths at 37 °C measured by the self-designed testing platform (Figure 6) which simulated the practical hemoperfusion process. The adsorption capacity decreased to 1.05 and 3.66 mg g\(^{-1}\) for carbonized and activated monoliths, respectively. For the activated monolith, not only the adsorption capacity but also the adsorption rate was much higher than the carbonized one, especially in the first hour. The results about the adsorption capacity for the monoliths acquired by this test platform were rather significant for this process was particularly close to practical clinical treatment. However, the adsorption performance should be further enhanced to bring the biomass-derived lotus root-like porous monoliths to practical applications.

**CONCLUSIONS**

With resourceful rice husks as the raw materials, lotus root-type monolithic AC was fabricated by the injection molding process followed by carbonization and activation. Besides millimeter-sized continuous channels, Brunauer–Emmet–Teller (BET) and mercury intrusion tests indicated that micro, meso, and macropores were also introduced in the wall of the channels after carbonization and activation. BET tests showed that the pore volume and specific area of the monolithic sample were about 1.28 mL g\(^{-1}\) and 329 m\(^2\) g\(^{-1}\), respectively. Adsorption capacity of VB12, the representative of middle molecular toxins in human blood, was about 3.66 mg g\(^{-1}\) based on a specially designed testing platform which simulated the practical clinical hemoperfusion process. The continuous channels in the lotus root-like monoliths could not only lower the pressure drop but also avoid detrimental collisions between the hemocytes and the adsorbents during the blood purification process. The micro, meso, and macropores in the channel walls could be further developed and modified to promote the adsorption capacity and selectivity, and thus the lotus root-type monolithic AC with a hierarchical porous structure derived from rice husks would be the promising candidate as adsorbents in hemoperfusion.

**MATERIALS AND METHODS**

**Materials and Preparation.** Rice husks, one of the extensive biomaterials with the natural porous structure, were chosen as the raw material. First, rice husks were precarbonized in an inert atmosphere at 850 °C. Then, after the carbonized rice husks were mixed with powdery CMC, which was used as the binder, they were further grinded to get a more uniform dispersion and smaller particle size.

| thermal treatment | mesopore volume (cc/g) | micropore volume (cc/g) | total pore volume (cc/g) | surface area (m\(^2\)/g) |
|-------------------|------------------------|-------------------------|--------------------------|--------------------------|
| carbonization     | 0.135                  | 0.068                   | 0.608                    | 168                      |
| activation        | 0.403                  | 0.135                   | 1.282                    | 329                      |

Figure 4. Adsorption capacity of VB12 at 37 °C for the monoliths after carbonization and activation at 37 °C.

Figure 5. Fabrication process of the lotus-type monolithic AC.
Subsequently, the powdery mixture was extruded to regular lotus root-type monolith via an injection molding machine under 6 MPa at room temperature after the mixture was sprinkled with a certain amount of deionized water. Then, to remove the binder, the monolith was carbonized in an inert atmosphere at 850 °C once again. Finally, the carbonized monolith was activated by 10 wt % sodium hydroxide (NaOH) aqueous solution, and it was further cleaned by diluted hydrochloric acid and deionized water until the washing water was neutral. The whole process is illustrated in Figure S, and it should be emphasized that the activation treatment was taken not only to decrease the content of silicon but also to develop micro and mesopores in the long channel walls. The monolithic block could be cut into small pieces with any length needed.

**Characterization.** The morphology and microstructure of the lotus root-type monolithic AC were characterized by scanning electron microscopy (SEM, Gemini SEM 500 from Zeiss), Raman examination (LabRAM HR Evolution from HORIBA Jobin Yvon) with a 532 nm laser light source was used to check the graphitization degree of the powders. Meanwhile, FTIR (X70 from NETZSCH) spectroscopy and XPS (250XI from Thermo Fisher Co.) were adopted to examine the chemical bonds and the chemical composition. Nitrogen adsorption (QUADRASORB SI-MP) and mercury intrusion (AutoPore IV 9500) tests were performed to investigate the pore structures, including specific surface area and the size distribution of the meso, micro, and macropores. The pore distributions were calculated by the DFT method (N_{2} at 77 K on carbon, slit/cylindrical pores, QSDFT equilibrium model) and the BET method.

**Adsorption Testing.** VB_{12} (Shanghai DiBai biotechnology Co., Ltd.), with the molecular weight of 1355 Da, was employed as the representative of middle molecular toxins in human blood to assess the adsorptive capacity of the porous samples. Different from previous work, in this study, a set of the in vitro testing platform, which simulated the practical hemoperfusion process, was specially designed to measure the actual adsorption capacity of the monolithic adsorbent in the chamber of a hemoditoxifier (Figure 6). The platform included 1000 mL VB_{12} aqueous solution (80 mg L^{-1}) keeping at 37 °C in the water bath, a peristaltic pump, and a self-made hemoditoxifier, in which a segment of lotus root-type sample with the diameter of about 50 mm was put in. VB_{12} aqueous solution was circulated in the platform at the rate of 200 mL min^{-1} with the help of a peristaltic pump just like the practical hemoperfusion clinical treatment. The dynamic adsorption was continued for 2 h, and the duration was just the same as a single clinical treatment. The variations of VB_{12} solution concentration were detected by an ultraviolet–visible (UV–vis) spectrophotometer at the wavelength of 360 nm. The adsorption capacities were calculated by the following eq 1.

\[ Q = \frac{(C_{0} - C_{t})}{m} \cdot V \]  

(1)

where Q (mg g^{-1}) meant the adsorption capacity, and C_{0} and C_{t} were the concentration of the solution before and after being purified, respectively. Meanwhile, V and m were the volume of the solution and the weight of the adsorbent. Obviously, the adsorption capacity obtained by the aforementioned platform might be more valuable to clinical applications compared with that got by static adsorption in a shaking bath. Nevertheless, the adsorption capacity of the powdery raw material, such as the carbonized rice husks, which might cause blockage of the filter screen in the self-made hemoditoxifier or could not be intercepted by the filter screen and then “contaminated” the solution, could only be examined by a regular shaking bath platform. Powder (50 mg) was added to 30 mL of VB_{12} aqueous solution (80 mg L^{-1}) in an Erlenmeyer flask, and then the mixture was kept in the shaking bath at 37 °C and 120 rpm min^{-1} in the dark room for 2 h.

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