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Shaping powdered active carbons into monoliths without decreasing mesoporosity by using silica sol as binder

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ABSTRACT

Powdered active carbon (PAC) was converted into monoliths without decreasing mesoporosity by using silica sol as a binder. The effects of sol dosage on physical properties of monoliths were investigated. The results indicated that using the sol could make the monoliths possess higher mesopore volume ($V_{\text{meso-BJH}}$) and/or mesopore fraction ($V_{\text{meso-BJH}}/V_t$) than the PAC, due to the mesoporous framework formed by the sol in the presence of PAC. Increasing the sol dosage could elevate the $V_{\text{meso-BJH}}$ or $V_{\text{meso-BJH}}/V_t$ of monoliths. When the dosage was 3.0 mL, we obtained a crack-free, regularly-shaped, and water-stable monolith with a $V_{\text{meso-BJH}}$ of 0.41 mL/g, $V_{\text{meso-BJH}}/V_t$ of 78.8%, BET specific area of 657 m^2/g, and compressive strength of 1.7 Mpa. This research was favorable for preparing carbon-based mesoporous monoliths promising in removing large molecules from wastewater.

1. Introduction

Active carbon monoliths are applicable in various fields like catalysis [1] and gas separation [2], due to their properties like increased bulk density compared to PACs, good mechanical strength, and tunable pore structure. A commonly-used method for preparing active carbon monoliths involves extruding PACs with binders such as pitch [3], carboxymethylcellulose sodium [4–6], polyvinyl alcohol [4–6], phenolic resin [2,7], poly(furfuryl alcohol) [7], H_3PO_4-loaded sawdust [8], cement [9], and clay [10,11]. However, the use of these binders renders the mesoporosity of obtained monoliths lower than that of PACs, which hampers adsorption of large molecules and/or reduces adsorption rate.

Thus, this research aimed to convert PAC into monoliths without reducing mesopore volume or mesopore fraction. We found that the aim could be achieved readily by employing commercially-available silica-sol binder, which is widely used industrially but has not been utilized to shape PAC into monoliths without presence of assistant binders. The finding was considered attractive for facile preparation of value-added carbon-based mesoporous monoliths. It should be mentioned that reports on application of the obtained monoliths are not the aim of this research.

2. Experimental

Sawdust-derived PAC (SPAC, 0.048–0.074 mm) was bought from China Zhucheng Zhongli Corporation. Silica sol with a particle size of 10–20 nm, SiO_2 content of 25 wt%, and Na_2O content of <0.3 wt% was provided by Qingdao Mike Corporation.

To convert SPAC into monoliths, firstly, a desired quantity of silica sol (1.6, 2.2, or 3.0 mL) was diluted with distilled water until the volume of the obtained liquid reached 7.6 mL. Subsequently, 2.4-g SPAC was added into the liquid, followed by stirring for 3 min. The resultant mixture was irradiated with microwave at 119 W for about 10 min under intermittent stirring to yield a moldable mixture. Then, the mixture was pressed in a 2.0-cm inner-diameter cylindrical mold at about 540 N for 30 s to yield a coin-like monolith. After drying the monolith at 110 °C for 180 min, the sample was heated in a tube furnace (tube inner-diameter: 55 mm) at 380 °C for 60 min in flowing nitrogen (400 mL/min). The obtained monolith was denoted as Mx, where x meant silica sol volume used to prepare the monolith.

To make comparison, the preparation procedure for M1.6 was used to convert an ash-free glucose-derived char (<0.074 mm) into a monolith recorded as GM1.6. The glucose-derived char was

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produced by heating glucose at 650 °C for 90 min in flowing N_2 (100 mL/min). Additionally, we produced silica from the sol in the same way that M1.6 was prepared, except that neither addition of PAC nor compression of microwave-heated sample was performed.

Nitrogen adsorption/desorption isotherms at −196 °C of samples were obtained using a static volumetric analyzer (TristarII 3020, Micromeritics, USA). The isotherms were employed to obtain BET specific area (S_{BET}), mesopore surface area (S_{meso}), total pore volume (V_t), mesopore volume (V_{meso} and $V_{\mathrm{meso\text{-}BJH}}$), micropore volume ($V_{\mathrm{micro}}$), and pore size distributions, with the used methods presented in Text S1 of Supplementary material (SM). The surface morphology, chemical composition, bulk density, ash content, compressive strength, and methylene blue uptakes of samples were also studied, with the adopted methods described in the Text S1.

3. Results and discussion

Fig. 1a shows that M1.6 and M3.0 were regularly-shaped and visually crack-free, with their diameter and height being about 22 mm and 10 mm, respectively. Such morphologies were maintained after the two samples were shaken at 150 rpm for 12 h in a 250-mL conical bottle containing 160-mL water, indicating that the samples were water-stable. The compressive strength of the samples was in the range of 0.8 to 1.7 MPa, indicating that they could withstand some pressure. The compressive strength and regular shape indicated that SPAC had been converted into monoliths successfully. The successful conversion was attributable to the silica sol-derived framework which bound SPAC together. This explanation was supported by the availability of a monolith after M3.0 was ashed (Fig. 1b). To gain further insight into the framework, some samples were investigated using SEM. Fig. 1c showed that the M3.0 ash displayed agglomeration/aggregation of numerous particles with sizes of about 40–1000 nm. Similar morphology was observed for the sol-derived silica (Fig. 1e) and M3.0 (Fig. 1d), but not for SPAC (Fig. 1f) or its ash (Fig. 1g), indicating that the framework mainly resulted from the agglomeration/aggregation of particles with sizes of about 40 to 1000 nm derived from the silica sol. The EDX analysis (Fig. S2, SM) showed that the total contents for O and Si in selected zones of M3.0 ash were higher than 95.0 at.% whereas those for other elements including Na were below 3.6 at.%, suggesting that the framework mainly consisted of silica.

The adsorption/desorption isotherms of SPAC and monoliths (Fig. 2a) increased with increasing relative pressure and displayed hysteresis loops, indicating that the isotherms were type IV (IUPAC classification) and many mesopores were present in the four samples. The abundant mesopores and strong water-stability of the

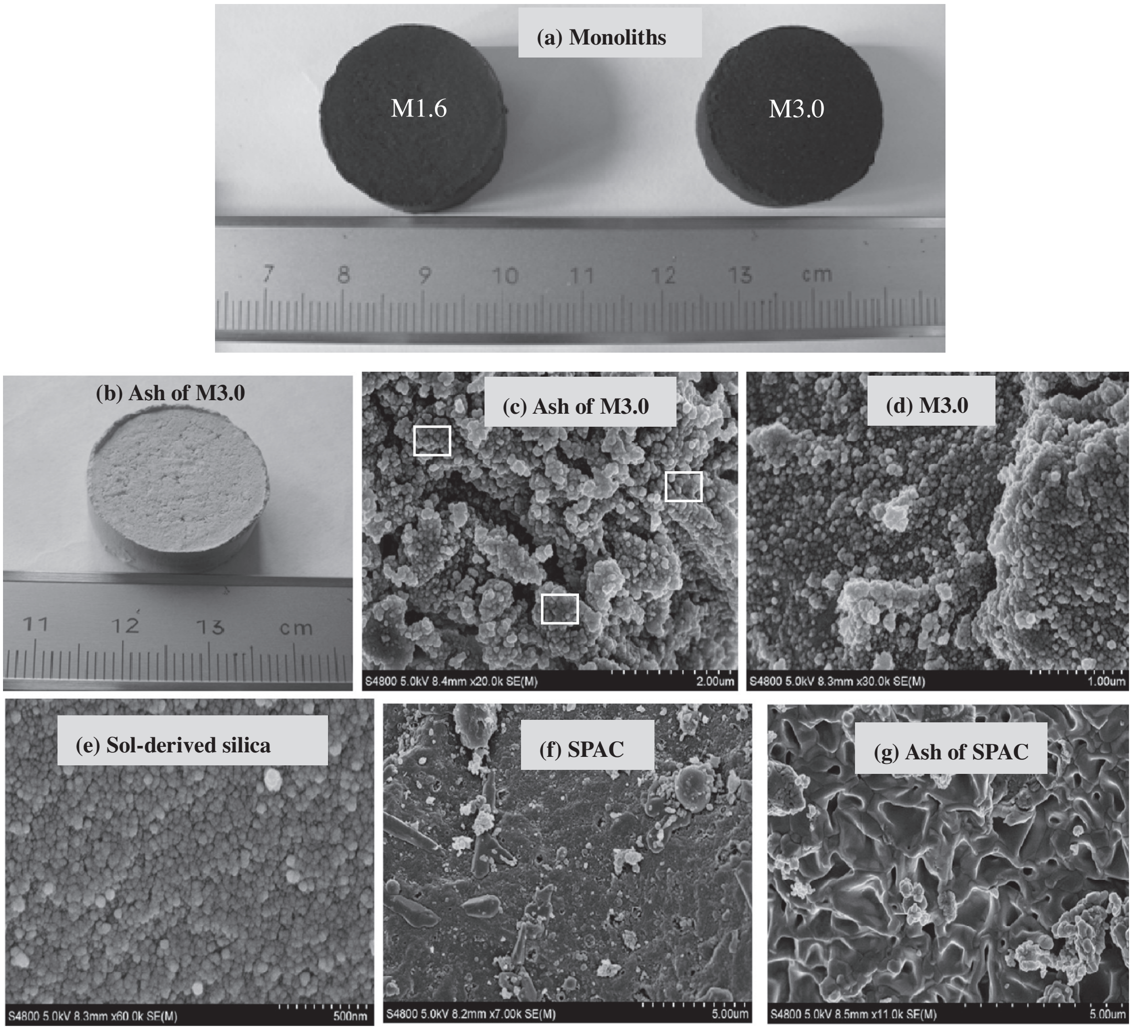

Fig. 1. Photographs for (a) monoliths and (b) ash of M3.0, and SEM images for (c) ash of M3.0, (d) M3.0, (e) sol-derived silica, (f) SPAC, and (g) ash of SPAC (The rectangles on figure (c) were the zones used for EDX analysis).