

Improving Adsorption Capacity of Ordered Mesoporous Carbon (OMC) Through Addition of Crosslink Agent

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ABSTRACT

High heteroatom content in carbon materials can improve the adsorption capacity for phenolic compounds from aqueous media. However, most work is focusing on the carbon material post-treatment. In this study, a straightforward and environmental-friendly method was proposed by incorporating nitrogen element in precursor through crosslink agent during polymerization process. A hard template synthesis route was employed using common mesoporous silica (SBA-15) as a template. Acrylamide and a crosslink agent were filled, polymerized and crosslinked within the mesopores. After carbonization and the removal of silica template, well-ordered mesoporous carbon material was obtained with a higher yield compared with the one without the crosslink agent. FT-IR, SEM and TEM were used to characterize the structures. The adsorption capacity for resorcinol removal was improved by crosslinking, and was 37% higher than commercial granular activated carbon.

Keywords: mesoporous carbon, SBA-15, phenolic, crosslink, adsorption capacity

1 INTRODUCTION

Ordered mesoporous carbon (OMC) materials have attracted growing attention due to their wide applications for catalyst supports [1, 2], electrode materials [3], and adsorbents [4]. OMCs have been thought as an excellent candidate for organic pollutants removal, due to their remarkable properties, such as uniform mesopores with tunable large diameters (typically in the range of 2-10 nm), high specific surface areas (SSA, up to 1800 m²g⁻¹) and higher hydrothermal resistance compared with mesoporous silica materials and other materials [5-7]. Since the first synthesis of OMC using sucrose as a carbon precursor [8], various carbon precursors have been explored, like polyacrylic acid [9], polypyrrole [10], polyacrylonitrile [11], and resorcinol-formaldehyde resin [12].

As one kind of the widespread pollutants in wastewaters, phenolic compounds are toxic and hazardous to aquatic life and human beings [5, 13, 14] even at very low concentration (0.1 μg/L) [15]. Thus, it is imperative to remove phenolic compounds from industrial wastewaters before discharging. Among all the methods for phenols and their derivatives removal, like oxidation, biodegradation,

membrane separation, precipitation, extraction and adsorption [13, 14, 16-18], adsorption was considered as the most effective method due to the sludge-free clean operation, acceptable price and easy availability of various adsorbents. Activated carbons are often used for phenolic compound removal [13, 14, 16] due to their good performance. However, activated carbon-based adsorbents are composed of large fraction of micropores (< 2nm), which can result in slow diffusion kinetics. Thus, OMCs with fast adsorption kinetics and high adsorption capacity are thought as undeniable substitutes for water purification.

In order to improve the adsorption capacity, a modified OMC was fabricated by Anbia and Ghaffari through coating CMK-1 with polyaniline [19]. He et al. [20] prepared modified CMK-3 through chemical oxidation by ammonium persulfate and H₂SO₄, and further grafted with 1-octanol using esterification reaction to enhance its adsorption performance. Guo et al. [9] imparted OMC with new oxygen containing groups through oxidation using concentrated nitric acid. All these methods, through incorporating functional groups or heteroatoms in the adsorbents, showed considerable adsorption performance improvement; however, post-treatments, either grafting or oxidation, can result in decrease of SSA and pore volume [9, 19, 20]. Also, the original structure can be damaged, especially shrinkage of pore size. In addition, post-modification can result in low bonding densities and blockage of mesoporous. Therefore, it would be a good choice to induce functional groups or heteroatoms in the carbon precursor before carbonization.

In this study, OMCs were fabricated through hard template synthesis using a common mesoporous silica template SBA-15. Three different ways were tried to incorporate nitrogen in the precursor for adsorption capacity improvement: 1) use concentrated sulfuric acid to fix nitrogen, 2) add melamine as a possible nitrogen source and 3) use nitrogen containing crosslink agent.

2 EXPERIMENTAL

2.1 Synthesis of Silica Template

The synthesis of SBA-15 was modified from literature [9]. Typically, 100 ml of concentrated hydrochloride acid (HCl, 37%) was added into 525 ml of distilled water to provide an acidic solution, and then 20 g of triblock

copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF) was added as surfactant to direct the formation of mesoporous structure. Subsequently, 46.5 ml of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added after the complete dissolving of above mixture. Then the resulting mixture was vigorously stirred to form a homogeneous solution. After the reaction at 50 °C for 6 h, the milky white suspension was cured in 90 °C water bath for 24 h. Then the solid product was filtered and washed using 2000 ml of 80–90 °C distilled water. After drying, the product was calcined in air flow furnace at 550 °C for 8 h.

2.2 Fabrication of OMCs

The synthesis of OMC was accomplished by in situ polymerization of acrylamide (AM) in silica mesoporous template. Typically, 10 g of AM ($\geq 99\%$, Aldrich) was mixed with 2g of completely ground SBA-15 powder in 20 ml distilled water. After the mixture was homogenous, 0.05g of 2, 2-azobisisobutyronitrile (AIBN, Aldrich) was added as a free radical initiator. The resulting mixture was then transferred into 65 °C water bath with continuous stirring for in situ polymerization. Afterwards, the PAM/SBA-15 composite was dried in oven at 200 °C overnight. Subsequently, the composite was carbonized at 700 °C under N₂ atmosphere for 8 h. After removal of silica template using hydrofluoric acid (HF, 48%, Aldrich) and washing with distilled water, OMC was dried in oven to obtain the final product, denoted as OMC-0. OMC-1 was obtained using above procedure, except the aqueous solution was composed of 10ml concentrated sulfuric acid (96.1%, HACH) and 10ml distill water. OMC-2 was fabricated as OMC-0 by adding 0.2 g of crosslink agent (N, N'-Methylenebisacrylamide) (ACROS ORGANIC) during polymerization process. OMC-3 was obtained by using the combination of above modified procedures. Based on the procedure for OMC-1, OMC-4 was obtained through mixing 2g of melamine (ACROS ORGANIC) in the aqueous solution.

2.3 Characterization

Transmission electron microscopy (TEM) was employed to characterize the mesoporous structure of SBA-15 and OMCs with acceleration voltage of 80 kV using a Hitachi 7600. SBA-15 was also observed under a JEOL 6300 Scanning Electron Microscopy (SEM). Functional groups and chemical bonds were detected by Fourier transform infrared spectroscopy (FT-IR) using a PerkinElmer Spectrum 100 FT-IR Spectrometer. Specific surface areas were obtained using a Micromeritics FlowSorb III Surface Area Analyzer.

2.4 Adsorption Study

Resorcinol was selected as a typical phenolic compound to evaluate the adsorption capacity of OMCs. Batch

adsorption experiments were conducted with the following procedure: resorcinol solution (100 ml) with concentration of 5mg/L was poured in both experimental (with adsorbent, OMCs) and control (without adsorbent, regarded as blank) conical flask; all the samples were placed in an E 24 Incubator Shaker (New Brunswick Scientific) at 200 rpm at room temperature; after 24 h, the conical flasks were removed and the solutions were filtered. The blank was used as reference to establish the initial concentration for the solutions containing OMCs. The filtered solution was analyzed for the final concentration of resorcinol. The residual concentrations were measured by Cary 50 UV-visible spectrophotometer (Varian) setting wavelength of 500 nm at room temperature. The amount resorcinol adsorbed by OMCs was determined with the following formula:

$$q = \frac{(C_i - C_f)V}{M} \quad (1)$$

Where, q is the adsorption capacity (mg/g); C_i is the initial concentration of resorcinol in solution (mg/L); C_f is the final concentration of resorcinol in treated solution (mg/L); V is the volume of the solution taken (L); M is the mass of the adsorbent OMCs (g).

3 RESULTS AND DISCUSSIONS

3.1 Morphology of SBA-15

The micro-structure of SBA-15 was exhibited in Figure 1, where a hexagonal framework can be observed. The rod-like silica template has an average diameter around 0.5 μm and a length of 0.8 μm.

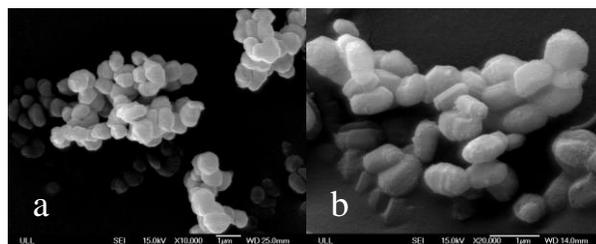


Figure 1: SEM images of SBA-15 under different magnifications (a $\times 8000$ and b $\times 20000$).

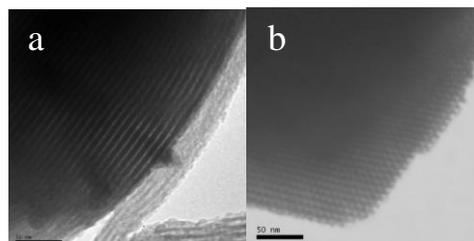


Figure 2: TEM images of SBA-15 seen from a) channel direction and b) perpendicular direction.

In order to observe the mesoporous structure, TEM images are shown in Figure 2. Ordered mesoporous structure was proved in Figure 2(a), with the average

channel diameter around 6.5 nm. Perpendicular view in Figure 2(b) displayed the hexagonal structure.

3.2 TEM Images of OMCs

The corresponding OMCs were duplicated from SBA-15 template with similar mesoporous structure, as illustrated in Figure 3. However, the channel diameter was a little smaller than the silica template, around 5 nm, which may result from the shrinkage of carbon/silica composite material during carbonization and removal of host [2, 10]. Comparing the OMCs using concentrated sulfuric acid (b, d, e) in Figure 3, it was noticed that the mesoporous structure became less uniform due to the complicated physical-chemistry effect of the concentrated H_2SO_4 , like dehydration carbonization and swelling. Even the perpendicular view in Figure 3 (f) shows that the hexagonal structure was not always as fine and smooth as its template, the ordered mesoporous structure was well preserved as previous reports [2, 9, 10].

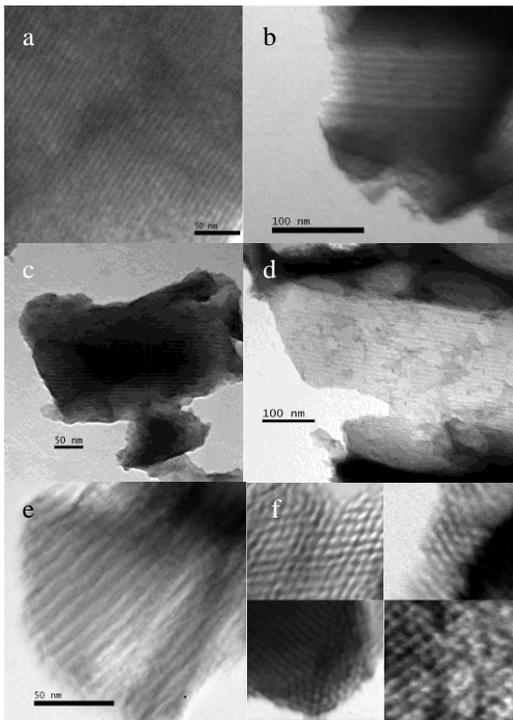


Figure 3: TEM images of OMCs: a) OMC-0, b) OMC-1, c) OMC-2, d) OMC-3, e) OMC-4, f) perpendicular view of OMCs.

3.3 Specific Surface Area of SBA-15 and OMCs

The SSA of silica template and OMCs were measured by N_2 adsorption-desorption method. The SSA of SBA-15 was $597 \text{ m}^2/\text{g}$. The SSA of OMC-0, 1, 2, 3 and 4 were 408, 376, 432, 432, and $416 \text{ m}^2/\text{g}$, respectively, close to previous study [9]. No significant difference was observed except lower SSA of OMC-2, which may decrease corresponding

adsorption capacity. Compared with silica templates, the SSA of OMCs decreased slightly as expected due to the shrinkage of the structure. The results show that the modification of carbon precursor has no obvious influence on the SSA of final OMC.

3.4 FT-IR Analysis

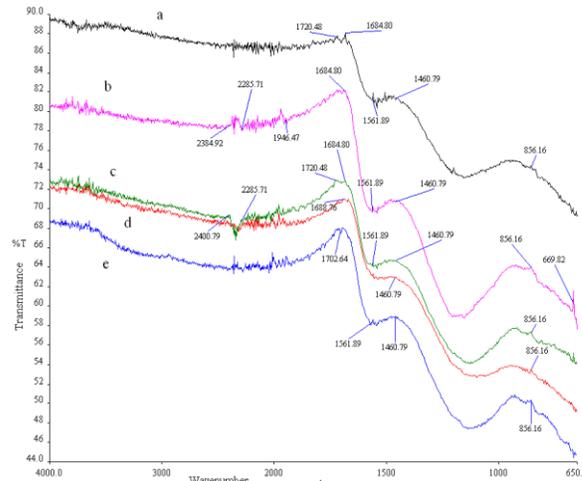


Figure 4: FT-IR spectra of (a) OMC-1, (b) OMC-4, (c) OMC-2, (d) OMC-3, and (e) OMC-0.

The FT-IR was used to detect the possible functional groups and changes attributed to the modifications of carbon precursor. As shown in Figure 4, the five OMCs displayed similar spectra: 1) weak small bands ranging from 3500 to 3950 cm^{-1} may result from the $-OH$ stretching vibration [3, 13, 16] due to the adsorption of moisture; 2) the strong peaks centered around 1700 cm^{-1} can be ascribed to $C=O$ [9, 20] resulting from PAM; 3) the bands near 860 cm^{-1} and between 1460 – 1560 cm^{-1} may be caused by the stretching vibrations of $C-H$ [16] and $C-N$ respectively [21]. Stronger waves were observed in (b, c, d) between 2285 and 2400 cm^{-1} , which may be assigned to $C-O$ [16], or some trapped N_2 [22] due to the pyrolysis of added chemicals. In (b), a sharp peak at 670 cm^{-1} was observed, which may be caused by $C-OH$ stretching vibration [23].

The results proved that adding crosslink agent can affect the structure of final OMC; however, the addition of H_2SO_4 and melamine were not obvious. The analyzed peaks reveal the existence of N, H, and O elements, which may enhance the interactions between adsorbent and pollutant to improve adsorption capacity through weak driving force like hydrogen-bond.

3.5 Adsorption Capacity Evaluation

The adsorption capacities for resorcinol removal were compared between OMCs and commercial granular activated carbon (GAC) (Norit). As shown in Figure 5, all the OMCs have higher adsorption capacity than GAC; OMC-2 and OMC-3 with crosslink agent show the highest adsorption capacity 37 mg/g , which is 37% higher than

GAC and close to previous reports [9, 24], suggesting the favorable influence of crosslink agent. The adsorption capacity of OMC-1 is slightly lower than OMC-0, meaning the single effect of H_2SO_4 is not good and may even damage the mesoporous structure (as shown in Figure 3b). Adding melamine (OMC-4) shows a little improvement, but it is believed better performance can be achieved by optimizing the dose and process.

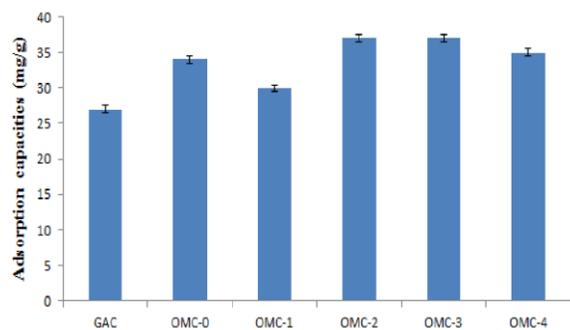


Figure 5: Comparison of adsorption capacities of GAC and OMCs.

Even in Figure 4, no obvious changes were observed through carbon precursor modification, the improved adsorption capacity may attribute to the increase of active sites like C-O and C-N bonds, which can drive the interaction between OMC and resorcinol through hydrogen-bond directly or indirectly [9, 16, 24]. In addition, it was observed that higher SSA of OMC may benefit the adsorption capacity.

4 CONCLUSION

Some attempts were tried to modify carbon precursors for improving adsorption capacity of OMCs. The TEM results show that precursor modification can preserve the ordered mesoporous structure well. Generally, adding crosslink agent and melamine exhibited good potential for adsorption capacity improvement. Although, using concentrated H_2SO_4 did not show adsorption capacity improvement directly, a higher yield (~40%) of OMC was noticed, which may attribute to the relative mild dehydration carbonization process. Also, yield was improved by adding crosslink agent, which may result from the carbonization of itself, and the crosslinking effect, which improved the molecular weight and reduced the pyrolysis of polymerized PAM. Even the improvement of adsorption capacity in this study was not significant, advantages of the developed OMC can be observed when the usage of adsorbent is scaled up, as well as the increase of the initial concentration of pollutants [14, 19, 24]. The FT-IR demonstrated the possible functional groups in the OMCs. Besides, it was found that specific surface area of OMC may play a crucial influence on the adsorption capacity.

This work provides a new avenue to fabricate OMCs with various functional groups and heteroatoms through modification the constituents or structure of carbon precursor. In the light of this research, it is possible to fabricate superior adsorbents suitable for removal of different pollutants through incorporating heteroatoms in carbon precursors.

5 ACKNOWLEDGEMENT

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