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Soft-templating synthesis of partially graphitic Fe-embedded ordered mesoporous carbon with rich micropores from bayberry kernel and its adsorption for Pb(II) and Cr(III)

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ABSTRACT

An eco-friendly promising strategy for the synthesis of biomass-derived ordered mesoporous carbon (BOMC) and Fe-doped BOMC (Fe/BOMC) using bayberry kernel as carbon precursor have been developed *via* liquidation and subsequent soft-templating synthesis. The obtained BOMC presents a 3D interconnected ordered mesoporous framework with big surface area. Spectroscopy analysis shows various Fe nanoparticles including zero Fe, Fe_2O_3 and Fe_3O_4 are successfully embedded, penetrating the interconnected micro/mesopore framework. Fe/BOMC still remains the ordered structure with high surface area ($1012 m^2/g$), mesopore volume ($0.95 cm^3/g$) and micropore volume ($0.35 cm^3/g$). Interestingly, the introduction of Fe increases the oxygen content and generates more oxygen-containing functional groups such as C=O group and C–O bands, which further enhances the active of adsorption sites, resulting in the higher adsorption of Pb(II) and Cr(III) on Fe/BOMC. The maximum adsorption amount of Pb(II) and Cr(III) adsorption increases by 18% and 21% to 123 mg/g and 46 mg/g, respectively. Moreover, 80% of the adsorption equilibrium amount is obtained at 15 min. The results demonstrate a cost-effective and environmental-friendly strategy for synthesizing bayberry kernel-derived Fe-doped ordered OMC with rich micro/mesopores, active iron and oxygen-containing functional groups for Pb(II) and Cr(III) adsorption.

1. Introduction

Due to the unique properties such as ordered channels, large pore volume, flexible framework composition and electrical conductivity, ordered mesoporous carbon (OMC) has aroused substantial research enthusiasm in application in many fields. Conventionally, phenols such as phenol, resorcinol and phloroglucinol, reacting with formaldehyde, have been widely utilized as carbon precursors for preparing OMCs *via* soft template method due to the formation of rigid polymer framework with three-connected covalent bonds [1]. For example, Zhao's group synthesized OMCs using phenol as carbon precursor [2]. Recent reports showed that resorcinol and phloroglucinol, having more reactive sites than phenol, can be utilized as precursor to assemble OMCs with 3-D cross-linked network. Moreover, using resorcinol or phloroglucinol as carbon precursors can increase the pore size of OMCs due to the less shrinkage of carbon framework by the achievement of higher polymerization degree [1]. Other groups also reported the successful synthesis of well-ordered OMCs by using resorcinol [3,4]. Recently, Kataoka et al. reported that the hydrophilic triphenol phloroglucinol is more appropriate than resorcinol to form a cubic structure of the OMCs [5].

Though widely used, phenols have some disadvantages such as deleteriousness and expensiveness. Meanwhile, the demand for OMCs is increasing. Therefore, taking into consideration of environmental friendliness, cost efficiency, sustainability, continuous availability and rapid regeneration, low-cost and natural biomass-based materials are more promising phenols-substituted carbon sources for OMCs [6,7]. Bayberry has large planting area with an annual yield of 400,000 tons in Zhejiang province of China. Despite accounting for over 10% of bayberry fruits' weight, bayberry kernels are keeping underutilized owing to limited effective ways. Recent reports showed that liquefaction in the presence of a catalyst has proved to be a good thermal chemical process to transform lignocellulosic material into much smaller molecules, which are composed of plentiful phenolic structures originating from the lignified portion of the plant cell wall. These phenolic-containing products for renewable biomass are potential to be

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the replacement of synthetically petroleum-derived phenols in preparing OMCs *via* the aforementioned soft-templating method.

Moreover, OMCs inlaid with Fe, Co, Ni nanoparticles have fascinating magnetic properties and applications such as magnetic separation. Simultaneously, composite materials of porous carbon immobilized nano-metal particles have proved to have more excellent adsorption ability [8]. Stable and interconnected frameworks of OMC with active pore surfaces are suitable for supporting other nanoentities, and consequently, for supporting Fe nanoparticles to design novel functional magnetic nanostructures with synergetic effects [9].

Though some methods have tried to fabricate OMCs from biomass [7,10], little research has reported on soft-templating synthesis of hierarchical Fe-doped OMC *via* biomass/surfactant self-assembly. Recently, Xu and co-workers, have successfully prepared ecotype phenol–formaldehyde resins using liquefied cornstalk as phenolic feed stocks [11]. Here, we speculated that biomass-derived phenol–formaldehyde resins could be the replacement of synthetically petroleum-derived phenols in preparing OMCs *via* soft-templating method.

Besides, heavy metals pollution has become a grave threat to human for the significant toxicity. Lead and chromium, the two most commonly used metals in industrial and agricultural production, exist widely in wastewaters [12,13]. It is reported that intake of lead and chromium even at very low concentration will cause deleterious effects on nervous, immune and reproductive system [14]. Many materials have been exploited to dispose the toxic ions, and OMC is considered as the most effective one for removing Pb(II) and Cr(III) by far.

Therefore, bayberry kernel was used as representative of biomass, and first liquefied into eco-friendly, environmentally biomass-based phenolic molecules and utilized as carbon precursor for the soft-templating synthesis of biomass-based OMC (BOMC), where tetraethyl orthosilicate (TEOS) was employed to enhance micropores. Iron magnetic nanoparticles were introduced on carbon framework through simple process-carbothermal reduction. Moreover, the effects of Fe doping on the morphology, textural and chemical characteristics were evaluated. The performance of the obtained OMCs before and after Fe doping in the removal of Pb(II) and Cr(III) were also investigated.

2. Materials and methods

2.1. Preparation of bayberry kernel-based resin

After grinding and screening through 50 mesh, 28 g bayberry kernel was liquefied with 13.5 g 36% diluted vitriol and 140 g phenol at 170 °C for 2 h under reflux, and about 150 g phenol liquefied bayberry kernel product was obtained. In the later experiment, 40.5 g phenol liquefied bayberry kernel product was employed and mixed with 6.5 g 20 wt.% NaOH solution under stirring for 10 min. Then 52.5 g 37 wt.% formaldehyde was dropwise added below 50 °C, and stirred for 100 min at 75 °C. The obtained mixture was cooled to room temperature, and subsequently, the mixture pH was adjusted to 5.0. Afterward, water was removed by rotary evaporation at 55 °C for 60 min. At last, the mixture was dissolved in 20 wt.% ethanol, and bayberry kernel-based resin ethanol solution was obtained.

2.2. Preparation of BOMC

To prepare BOMC, 8.0 g F127 and 5.0 g 0.2 mol/L HCl were dissolved in 40.0 g absolute ethyl alcohol and stirred for 1 h at 40 °C. Subsequently, 10.4 g TEOS and 25 g 20 wt.% bayberry kernel resin solution was added. After stirring for 2 h, the mixture was transferred into culture dishes to be evaporated at room temperature for 9 h, and thermopolymerized at 105 °C for 24 h. Next, the pale-yellow and transparent membrane was scraped and ground into fine flour. The calcination was performed at 350 °C for 3 h and 900 °C for 2 h with a heating rate of 1 °C/min under a 20 mL/min N_2 flow to obtain carbon product. Soon after NaOH etching, biomass-based carbon was obtained, marked BOMC.

2.3. Preparation of Fe-doped BOMC

The Fe-doped BOMC (Fe/BOMC) was prepared *via* carbothermic reduction using $Fe(NO_3)_3 \bullet 9H_2O$ as iron source. In typical preparation, 3 g BOMC and 10 mL n-hexane solvent were mixed to form a supernatant solution under stirring. Meanwhile, $Fe(NO_3)_3 \bullet 9H_2O$ was dissolved in 50 mL deionized water and then was dropwise added into the supernatant solution under magnetic stirring to be better impregnated. Subsequently, the mixture was carbonized at 350 °C for 3 h and 900 °C for 2 h with a heating rate of 1 °C/min under a 20 mL/min N_2 flow. After cooling and washing, Fe/BOMC sample was acquired.

2.4. Characterization

Nitrogen adsorption isotherms were employed to characterize surface area (S_{BET}), total pore volumes (V_{total}), HK micropore volume (V_{HK}), BJH mesoporous volume by Brunauer–Emmett–Teller, single point volume and Barrette–Joynere–Halenda method. Mesopore size distribution was obtained by BJH method. The morphologies were examined by scanning electron microscope (SEM, Hitachi S-3500NII) and transmission electron microscopy (TEM, JEOL, JEM-2100(HR)). Surface chemistry was measured *via* Fourier transform infrared spectrum (FTIR, Thermo Electron, Nicolet6700) and X-ray photoelectron spectroscopy (XPS, ESCALAB260XI, Thermo Scientific).

2.5. Adsorption experiments

Batch adsorption was performed to measure the adsorption capacities of Pb(II) and Cr(III) at pH 6.0 for 4 h at 150 rpm. In the experiments, 0.02 g of adsorbent was suspended in 100 mL solution containing different Pb(II) and Cr(III) concentrations from 1 to 100 mg/L, respectively. The effect of time on the adsorption was investigated by adding 0.10 g adsorbent in 500 mL solution with different contact times (0–160 min) at 25 °C. The solution samples were analyzed by A3 flame atomic absorption spectrophotometer. The equilibrium adsorption capacity (q_e, mg/g) was calculated by Eq. (1):

$$q_e = (C_0 - Ce)V/m^*1000 \quad (1)$$

where C_0 and C_e are initial and equilibrium concentration of heavy metals (mg/L), respectively; V is solution volume (mL), and m is adsorbent dose (g).

3. Results and discussion

3.1. Textural and structural characterization

As shown in Fig. 1a, BOMC and Fe/BOMC exhibit a steep initial uptake for nitrogen at low P/P_0, indicating the existence of micropores. The hysteresis loops at 0.40–0.92 *P/Po* demonstrate their mesopore structures. Fig. 1b shows that BOMC and Fe/BOMC possess bimodal mesopores with sizes at 2.37 nm and 4.95 nm, 2.50 nm and 4.96 nm, respectively. The S_{BET}, V_{total}, V_{HK} and V_{BJH} of Fe/BOMC are 1012m^2/g, 0.97cm^3/g, 0.35cm^3/g and 0.90cm^3/g (Table 1), respectively. Compared with BOMC, V_{HK} and V_{BJH} decreases 0.12cm^3/g and 0.20cm^3/g, respectively.

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