Journal of Colloid and Interface Science 424 (2014) 104–112

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Optimization of mesoporous carbons for efficient adsorption of berberine hydrochloride from aqueous solutions

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ARTICLE INFO

Article history:
Received 19 December 2013
Accepted 1 March 2014
Available online 12 March 2014

Keywords:
Mesoporous carbon
Pore texture optimization
Berberine hydrochloride
Adsorption

ABSTRACT

Sixteen mesoporous carbon adsorbents were synthesized by varying the ratio of soft to hard templates in order to optimize the pore textural properties of these adsorbents. The mesoporous carbon adsorbents have a high BET specific surface area (1590.3–2193.5 m^2/g), large pore volume (1.72–2.56 cm^3/g), and uniform pore size distribution with a median pore diameter ranging from 3.51 nm to 4.52 nm. It was observed that pore textural properties of the carbon adsorbents critically depend on the molar ratio of carbon sources to templates, and the hard template plays a more important role than the soft template in manipulating the pore textures. Adsorption isotherms of berberine hydrochloride at 303 K were measured to evaluate the adsorption efficacy of these adsorbents. The adsorption of berberine hydrochloride from aqueous solutions on the sixteen mesoporous carbon adsorbents synthesized in this work is very efficient, and the adsorption equilibrium capacities on all samples are more than double the adsorption capacities of berberine hydrochloride of the benchmark adsorbents (polymer resins and spherical activated carbons) at similar conditions. It was observed from the adsorption experiments that the equilibrium adsorption amounts of berberine hydrochloride are strongly correlated with the BET specific surface area and pore volume of the adsorbents. The adsorbent with the highest BET of 2193.5 m^2/g displayed the largest adsorption capacity of 574 mg/g at an equilibrium concentration of 0.10 mg/mL of berberine hydrochloride in an aqueous solution.

Introduction

Berberine hydrochloride, an isoquinoline derivative alkaloid, widely exists in medicinal herbal plants. Berberine hydrochloride has a variety of pharmacological effects such as anti-tumor activity, anti-biotic property, anti-oxidant, anti-inflammatory effects; it has been used for the treatment of gastroenteric discomfort and therapy of diabetes in clinic [1–5]. Generally, berberine hydrochloride is obtained from extracts of herbal plants along with a large amount of coexisting impurities. For further purification of berberine hydrochloride, a series of cumbersome steps such as dissolving, filtration, re-crystallization and column separation are needed. This approach is time-consuming, and high purity is still very difficult to achieve by using traditional methods due to the large number of impurities coexisted in herbal plant extracts [3]. Therefore, effective separation and purification of berberine hydrochloride from herbal material extracts is a very challenging task.

Adsorption process for separation and purification of natural products like berberine hydrochloride from herbal plant extracts is believed to be widely used, effective and simple to operate. Some commercial adsorbents including silica gel (SiO_2), alumina (Al_2O_3), activated carbon, polymer resins and minerals such as bentonites and zeolites have been used for purifying natural products [6–10]. However, high adsorption capacity, high selectivity and efficient regeneration are difficult to achieve on these conventional adsorbents. Development of effective adsorbents with high adsorption capacity, high selectivity and efficient regeneration is an exciting task.

The properties of mesoporous carbons such as high specific surface areas, large pore volume, regular and tunable pore structures, along with good mechanical stability [11,12] make these materials an attractive adsorbent. Mesoporous carbon materials have been proven to be very efficient as adsorbents for adsorptive

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http://dx.doi.org/10.1016/j.jcis.2014.03.012
0021-9797/

removal of environmental pollutants such as organic compounds from wastewater [13–17] and adsorptive purification of biomolecules from aqueous solutions [18,19]. Normally, mesoporous carbons can be produced through the hard template [20–23] or the soft template approaches [24–27]. For the hard template route, suitable monomer or polymer carbon precursors are introduced into the pores of a hard template like mesoporous silica with a controlled structure, after cross-linking and thermal carbonization of the organic precursors and the removal of the silica template by a sodium hydroxide or hydrofluoric acid solution, mesoporous carbon is produced. For the soft template approach, a thin film containing amphiphilic molecules such as surfactants and block copolymers as soft template and phenolic resins as the carbon precursor is synthesized from the organic–organic self-assembly method induced by solvent evaporation, and mesoporous carbon is produced after carbonization. Triblock copolymers Pluronic F-127 and P-123 are two commonly used soft templates [28–30] for adjusting the pore size of mesoporous carbons. Our previous study of adsorption of alkaloid compounds on mesoporous carbons [31] has suggested that mesoporous carbon is a promising adsorbent for effective adsorption and purification of berberine hydrochloride from the extracts of herbal plants. However, limited experimental data are currently available about the adsorption of natural products such as berberine hydrochloride on mesoporous carbons [31], and no literature is available about the relationship between pore textural properties of mesoporous carbons and their adsorption properties for berberine hydrochloride, which is essential for identifying suitable mesoporous carbon adsorbents.

The main objective of this work was to explore the effect of the precursor composition on the pore textures of mesoporous carbon adsorbents, to establish the relationship between the pore textural properties of mesoporous carbons and adsorption properties for berberine hydrochloride, and to identify suitable mesoporous carbon adsorbents for this application. Sixteen mesoporous carbon adsorbents were synthesized, characterized, and evaluated for adsorption of berberine hydrochloride from aqueous solutions by batch adsorption equilibrium experiments. The adsorption results obtained were compared with those on traditional macroporous resin and spherical activated carbon adsorbents.

Experimental

Materials

The triblock copolymer Pluronic F127, tetraethyl orthosilicate (TEOS, >99% purity), and formaldehyde solution (36.5–38 wt%) were obtained from Sigma–Aldrich, and Berberine hydrochloride (>98% purity) was purchased from Shanghai Darui Finechem Ltd. (Shanghai, China), AR grade ethanol, phenol, HF, HCl, NaOH were from Sinopharm Chemical Reagent Co., Ltd. All these materials were used without further purification.

The main properties of berberine hydrochloride including molecular structure, molecular weight and molecular size, optimized molecular structure performed by the Gaussian 09 software package are listed in Table S1 in the Supplementary document.

Synthesis of the mesoporous carbons

The mesoporous carbon adsorbents were synthesized following a similar procedure described in the literature and our previous work with a minor modification [14,24,32,33].

Synthesis of resol precursors

A soluble phenolic resin resol was synthesized from phenol and formaldehyde solution in a base-catalyzed process. 24 g of phenol was melted at about 40 °C in a flask, 1.02 g of 20 wt% NaOH aqueous solution was then added into the melted phenol and the solution was mixed with 15.72 g of formaldehyde solution under stirring. After being stirred for 1 h at 70 °C, the mixture was then cooled to room temperature. The pH of the mixture was adjusted with a 2 mol/L HCl solution to about 7, and water was removed at 35 °C in a vacuum oven. The final product was dissolved in ethanol to obtain a 20 wt% phenolic resin resol ethanolic solution.

Synthesis of mesoporous carbons

The mesoporous carbon samples were synthesized with the preformed phenolic resin resol solution as a carbon resource, and tetraethyl orthosilicate (TEOS) and triblock copolymer F127 as templates in an ethanol solution. The synthesis compositions were in the range of phenol/formaldehyde/F127/TEOS (molar ratio) = 1:0.75:0.10:1.0 – 1:0.75:0.25:1.6, and the detailed compositions are listed in Table 1. In a typical preparation, 1.73 g of tetraethyl orthosilicate (TEOS) was pre-hydrolyzed in the presence of 1.0 g of 0.2 mol/L HCl and 4.0 g of ethanol at room temperature for 5 h, 5.0 g of 20 wt% preformed phenolic resin resol solution, 1.6 g of F127 and 8.0 g of ethanol were then added into the mixture under stirring for about 10 min until F127 was completely dissolved, and a homogeneous solution was obtained. After that, the solution was poured into an uncovered petri dish to evaporate ethanol at room temperature for about 12 h, then held at 100 °C in a muffle furnace for 24 h. The transparent film obtained after those steps was loaded in a quartz boat for calcination in a nitrogen atmosphere with a flow rate of 70–100 cm^3/min. Calcination was carried out in a tubular

Table 1
The main properties and the synthesis compositions of the mesoporous carbons.

Samples	Molar ratio of (phenol:formaldehyde:F127:TEOS)	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Sample 1	1:0.75:0.10:1.0	1590.3	1.85	4.20
Sample 2	1:0.75:0.10:1.2	1832.9	1.90	3.77
Sample 3	1:0.75:0.10:1.4	2083.9	2.09	3.74
Sample 4	1:0.75:0.10:1.6	2193.5	2.12	3.51
Sample 5	1:0.75:0.15:1.0	1892.2	2.34	4.30
Sample 6	1:0.75:0.15:1.2	1981.3	2.42	4.18
Sample 7	1:0.75:0.15:1.4	1860.7	2.20	3.99
Sample 8	1:0.75:0.15:1.6	1977.5	2.18	3.69
Sample 9	1:0.75:0.20:1.0	1632.1	1.75	3.74
Sample 10	1:0.75:0.20:1.2	1949.8	2.54	4.52
Sample 11	1:0.75:0.20:1.4	1919.6	2.56	4.28
Sample 12	1:0.75:0.20:1.6	1973.9	2.42	3.94
Sample 13	1:0.75:0.25:1.0	1827.2	1.79	3.61
Sample 14	1:0.75:0.25:1.2	1760.9	1.82	3.60
Sample 15	1:0.75:0.25:1.4	1913.7	2.39	4.21
Sample 16	1:0.75:0.25:1.6	1778.9	1.72	3.57