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Adsorption of alkaloids on ordered mesoporous carbon

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ABSTRACT

An ordered mesoporous carbon (OMC) adsorbent was synthesized, characterized, and evaluated for effective separation and purification of alkaloid compounds from aqueous solutions. The OMC adsorbent has a large BET specific surface area (1532.2 m^2/g), large pore volume (2.13 cm^3/g), and narrow pore diameter distribution with a median pore diameter of 4.21 nm. Berberine hydrochloride, colchicine, and matrine were selected as the model compounds for evaluating the adsorption properties of the OMC adsorbent for alkaloid purification. Batch adsorption experiments of pure components in water were carried out to measure both adsorption equilibria and kinetics, and column breakthrough and desorption experiments were performed to validate the separation and regeneration efficacy of the OMC adsorbent. The adsorption equilibrium capacities of berberine hydrochloride, colchicine, and matrine on the OMC adsorbent at 0.100 mg/L and 298 K are 450, 600, and 480 mg/g, respectively, which are more than double the adsorption capacities of these compounds on two commonly used commercial resins (HPD300 and HPD100B) at similar conditions. Adsorption equilibrium of all three alkaloids could be obtained within 120 min at 298 K. The dynamic adsorption capacities determined from the breakthrough experiments are within 12% of the estimated equilibrium capacities from the Langmuir isotherms; and 74.3–92.8% of the adsorbed amounts could be recovered by desorbing with a 70% alcohol solution. The adsorption isotherms are analyzed with both Langmuir and Freundlich models, the adsorption kinetic data with the pseudo-first-order and pseudo-second-order models, and the breakthrough curves with four breakthrough models. The large adsorption capacity, fast adsorption rate, and easy regeneration make the ordered mesoporous carbon a promising adsorbent for adsorption and purification of alkaloid compounds from the extracts of herbal plants.

1. Introduction

Alkaloids, an important class of pharmaceutical compounds, are a group of natural organic compounds containing mostly basic nitrogen atoms in a heterocyclic ring [1]. To date, over 10,000 alkaloids have been isolated from natural products, and the number of alkaloids is increasing by 100 per year [2,3]. Alkaloids are known to derive from at least 186 families, 173 genera, and 7231 species of plants [3] and usually subdivided into protoalkaloids, truealkaloids, and pseudoalkaloids [3,4]. Alkaloids have a variety of biological and pharmacological activities such as antiviral [5], antitumor [6,7], antioxidant [8,9], anti-inflammatory [8,10], antinociceptive, antipyretic [10], and so on. Many of the alkaloids are the main bioactive ingredients of herbal medicines, which have been therapeutically used to treat various diseases for several decades [2]. Berberine hydrochloride, colchicines, and matrine are three typical alkaloids that belong to the isoquinoline derivative, pyrazine derivative, and pyridine derivative alkaloids, respectively. They have a wide range of biological activities and pharmacological effects [7,9,11,12], and berberine hydrochloride and matrine are two main effective components of some Chinese traditional medicines [13,14].

Generally, alkaloids are obtained from natural resources along with a large amount of coexisting impurities using chemical solvent extraction. The low concentration and structural diversity of alkaloids make their separation and purification a very challenging task. Different physical and chemical methods have been applied in separation and purification of alkaloids including crystallization, precipitation [15], liquid–liquid extraction, membrane filtration [16], adsorption [17–20], ion-exchange [21,22], and chromatography methods such as gas chromatography [13], liquid chromatography [23–25], centrifugal partition chromatography [26], and high-speed counter-current chromatography [2,27–29]. Among these methods, adsorption process for separation and purification of alkaloids is widely used, quite effective, and simple to operate. Silica gel (SiO_2), alumina (Al_2O_3), activated carbon, and polymer resins are the commonly used adsorbents for purifying alkaloids

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in a chromatography column [17–19]. However, high adsorption capacity and selectivity are hard to achieve by using these traditional adsorbents; development of effective adsorbents with both high adsorption capacity and selectivity is an exciting and challenging task.

Due to its unique and tunable pore structures, high surface areas and mechanical stability, ordered mesoporous carbons have been proven to be a kind of efficient adsorbents for adsorptive removal of environmental pollutants such as aromatic compounds and dyes from aqueous solution [30–34]. Ordered mesoporous carbons are normally produced through a template approach [33,35–38] or direct synthesis method [32,39–41]. For the template approach, suitable carbon precursors are introduced into the ordered pores of a hard template like mesoporous silica, after thermal carbonization and removal of the silica wall by a hydrofluoric acid or sodium hydroxide solution, ordered mesoporous carbon is produced. For the direct synthesis method, a thin film containing amphiphilic surfactants as soft template and phenolic resins is produced from the self-assembly method in an ethanol solution and ordered mesoporous carbon is produced after carbonization. Triblock copolymers such as Pluronic F-127 and P-123 are the two common amphiphilic surfactants used as the soft templates [40,42–44], and the size of the mesopores can be adjusted by changing templates. According to the properties especially the tunable pore size of ordered mesoporous carbons, it may have the potential to be a kind of effective adsorbents for selective separation and purification of alkaloids from aqueous solutions. However, no literature is currently available about adsorption of natural products such like alkaloids on ordered mesoporous carbons.

The main objective of this work was to explore the feasibility of using ordered mesoporous carbon as an effective adsorbent for purifying alkaloids. An ordered mesoporous carbon adsorbent was synthesized, characterized, and evaluated for adsorption of alkaloids from aqueous solutions for the first time. Berberine hydrochloride, colchicine, and matrine were chosen to be three model alkaloid compounds. Adsorption isotherms, kinetics, and dynamic breakthrough curves were performed and analyzed in detail. These results were also compared with those obtained on traditional macroporous resin adsorbents.

2. Experimental

2.1. Materials

The triblock copolymer Pluronic F127, tetraethyl orthosilicate (TEOS, >99% purity), and formaldehyde solution (36.5–38 wt%) were purchased from Sigma–Aldrich, and AR grade phenol, ethanol, HF, HCl, NaOH were from Sinopharm Chemical Reagent Co., Ltd. All these materials were used as received.

Berberine hydrochloride was purchased from Shanghai Darui Finechem Ltd. (Shanghai, China), colchicine was provided by Nanjing Zelang Medical Technology Co., Ltd. (Nanjing, China), and matrine was purchased from Shanghai Tauto Biotech Co., Ltd. (Shanghai, China); they all have purity higher than 98%, and they were used without any purification. Their main properties including molecular structure and molecular weight were listed in Table 1. HPLC grade methanol was obtained from Merck.

2.2. Synthesis of the ordered mesoporous carbon

The ordered mesoporous carbon adsorbent was synthesized following an established procedure [30,39] with a minor modification [45,46].

Synthesis of Resol Precursors. A soluble phenolic resin resol was prepared from phenol and formaldehyde solution in a base-catalyzed process. 8 g Of phenol was melted at about 40 °C in a flask and mixed with 0.34 g of 20 wt% NaOH aqueous solution; 5.24 g of formaldehyde solution was then added to this solution under stirring. The mixture was hold at 70 °C upon further stirring for 1 h and then cooled to room temperature. The pH of the mixture was adjusted to about 7 with a 2 M HCl solution, and water was removed in a vacuum oven at 35 °C. The final product was dissolved in ethanol to form a 20 wt% phenolic resin resol solution.

Synthesis of Mesoporous carbons. 31.2 g of tetraethyl orthosilicate (TEOS) was pre-hydrolyzed in the presence of 15.0 g of 0.2 M HCl and 60.0 g ethanol for 5 h at a room temperature. 75.0 g of 20 wt% preformed phenolic resin resol, 24.0 g of F127, and 120.0 g of ethanol were then added into the mixture under stirring until F127 was completely dissolved, and a clear solution was obtained. After that, the mixture was poured into an uncovered petri dish to evaporate the ethanol at room temperature for about 12 h and then heated in a muffle furnace at 100 °C for 24 h. A transparent film obtained after those steps was loaded in a quartz boat and calcined in a tubular furnace in a nitrogen atmosphere. Calcination was carried out at 350 °C for 5 h to remove the triblock copolymer template, followed with a carbonization step at 900 °C for 4 h (with a heating rate was 1 °C/min). The product was immersed in 10 wt% HF solution at room temperature for 24 h to remove the silica component, then filtrated, washed with de-ionized water to a neutral pH, and then dried at 100 °C for 24 h. The final template-free carbon product was crushed into powders before use, and the particle diameter was controlled between 0.18 and 0.45 mm.

2.3. Characterization of the ordered mesoporous carbon

The BET specific surface area, pore volume, and pore diameter distribution of the mesoporous carbon adsorbent were determined by measuring the N_2 adsorption–desorption isotherms at 77 K in a Micromeritics ASAP 2020 surface area and porosimetry analyzer. Prior to the adsorption measurement, the carbon sample was degassed under a vacuum at 573 K for approximately 6 h. By using the Micromeritics ASAP 2020 built-in software, the pore textural properties including BET specific surface area, pore diameter distribution, and pore volume were calculated. Transmission electron microscopy (TEM, Joel JEM-2100F) was used to image the mesoporous structures in the OMC sample. Raman spectroscopy was carried out using the 632.8 nm (1.96 eV) laser excitation on a Renishaw inVia Raman microscope, and the FT-IR spectroscopy was obtained from a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer. The small angle X-ray diffraction (XRD) was performed with a Rigaku D/max 2550/PC X-ray diffractometer equipped with a Cu Kα source.

2.4. Analysis of alkaloid model compounds

An Agilent 8453 UV–visible spectroscopy system was used to determine the concentrations of berberine hydrochloride, colchicine, and matrine in their aqueous solutions at the wavelength of 345, 353, and 210 nm, respectively.

An Agilent 1100 liquid chromatographic system was used to determine the concentrations of berberine hydrochloride, colchicine, and matrine from the mixture solution. The HPLC has a Phenomenex-C18 (250 mm × 4.6 mm, 5 μ) column. The flow rate was set at 0.6 mL/min, and the column temperature was maintained at 30 °C for the analysis. The mobile phase, detection wavelength, calibration curves, and linear ranges for the three alkaloid model compounds were listed in Table S1. The HPLC profile of an alkaloid mixture sample is displayed in Fig. S1.