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Synthesis and characterization of cubic mesoporous bridged polysilsesquioxane for removing organic pollutants from water

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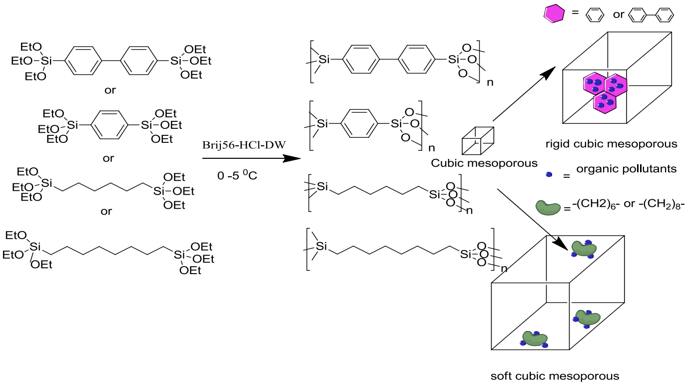
HIGHLIGHTS

- 3D cubic mesoporous BPS were successfully synthesized and characterized.
- Hydrophobic interaction dominantly controlled organic pollutants' sorption on BPS.
- Rigid aromatic BPS showed a higher sorption capacity than soft aliphatic BPS.
- 3D cubic mesoporous BPS show high sorption capacity and easy regeneration.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexane, octane, phenyl, and biphenyl-bridged bis(triethoxysilyl) precursors were used in synthesizing cubic mesoporous bridged polysilsesquioxane (BPS) copolymers. Structural characterization was carried out by FTIR, small angle XRD, Brunauer–Emmett–Teller-N_2 sorption, ^{1}H NMR, and TEM. We successfully synthesized both "rigid" and "soft" 3D cubic mesoporous BPS with high surface area and pore volume, as attested by the comprehensive characterization data. Adsorption of pyrene, phenanthrene, nitrobenzene, and 2,4-dichlorophenol on BPS was greatly affected by adsorbate properties, i.e., K_{ow}, solvation properties and molecular size. Hydrophobic interaction dominantly controlled organic pollutants' sorption on BPS. Other interactions, e.g., π–π and H-bond interactions, also have effects on sorption as indicated by K_{ow} normalized sorption isotherms. Rigid aromatic BPS (phenyl and biphenyl) showed a higher sorption capacity than soft aliphatic BPS (hexane and octane). A conceptual model was proposed to further explain the phenomena. This study suggests a promising application of cubic mesoporous BPS in wastewater treatment.

1. Introduction

Pollution from organic compounds has become one of the most serious global environmental issues today. Organic pollutants once released into the aquatic ecosystem can cause various environmental problems, which include clogging sewage treatment plants, adversely affecting on the aquatic biota, increasing biochemical oxygen (Wang et al., 2010a). Therefore, how to deal with wastewater that contains organic pollutants is gaining more and more attention.

Current technologies for wastewater treatment include ozonolysis (Beltran et al., 1992), photolysis (Yu et al., 2012), photocatalytic decomposition (Ide et al., 2012), adsorption (Kato et al., 2008; Merle et al., 2010), membrane filtration (Yang et al., 2012)

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and biological treatment (Nurisepehr et al., 2012). Among those technologies, adsorption by sorbents such as carbon nanotubes (Yang et al., 2006a,b; Wang et al., 2008), rice husk ash (Jang et al., 2009), activated carbon (Kato et al., 2008) and hydrophobic zeolite (Merle et al., 2010) is regarded as one of the most commonly used methods. Although many studies have been conducted on sorption, there are still some shortcomings needed to be addressed, e.g., low sorption efficiency, high cost, selective sorption, and difficult regeneration (Bercic et al., 1996; Matatov-Meytal and Sheintuch, 2000). More novel adsorbents are thus required to solve these problems.

Surfactant templated hybrid mesoporous sieves with molecular-scale mixing of inorganic and organic species inside pore walls have been synthesized and studied by three research groups (Asefa et al., 1999; Inagaki et al., 1999; Melde et al., 1999; Yoshina-Ishii et al., 1999). Such materials are made by combining surfactants with $(R'O)_3Si–R–Si(OR')_3$ precursors that are used in the fabrication of bridged polysilsesquioxanes (BPS) (Small et al., 1993; Loy and Shea, 1995). Bridging groups that have appeared in hybrid cubic and hexagonal structures of BPS include methane (Inagaki et al., 1999; Melde et al., 1999), ethane (Asefa et al., 1999; Melde et al., 1999), hexane (Whitnall et al., 2005), amido (Lin et al., 2011), octane (Tan et al., 2007), phenyl (Cho et al., 2009) and biphenyl (Kapoor et al., 2002). Because of mesoporous structure, BPS is suggested to be a potential sorbent. In addition, different organic bridging groups can create favorable surface-organic pollutants interactions, which can further enhance adsorption capacity of BPS. Burleigh et al. (2002) studied phenols' sorption on arylene- and ethylene-BPS, and concluded that BPS was a candidate sorbent for the removal of phenols due to its high adsorption capacities, fast adsorption kinetics and easy regeneration. However, their study is limited in two dimensional structural BPS. BPS also has cubic structure. Cubic structure with interpenetrating networks of pores exhibits higher activity than two dimensional hexagonal structures (Peng et al., 2012). Hence we hypothesize that cubic structure BPS adsorbs more organic pollutions from wastewater than hexagonal structural one.

We describe herein the synthesis and characterization of cubic mesoporous structure BPS and its application as a sorbent for the removal of organic pollutants. Four different bridging groups, two soft and aliphatic (hexane and octane) and two rigid and aromatic (phenyl and biphenyl) were used which will inevitably increase the hydrophobicity of BPS to different extents. Phenanthrene, pyrene, nitrobenzene and 2,4-dichlorophenol were selected to represent organic pollutants. The specific objectives of this study therefore were: (a) synthesize and characterize cubic mesoporous structure BPS with different bridging groups, (b) compare sorption ability of different bridged BPS and (c) study the influence of adsorbate properties on adsorption.

2. Experimental

2.1. Materials

1,8-Bis(triethoxysilyl) octane (BESO), 1,4-Bis(triethoxysilyl) phenyl (BESP), 4,4′-Bis(triethoxysilyl) biphenyl (BESB), polyethylene glycol monocetyl ether, $n = 23$ (Brij 56), unlabeled pyrene (99+%), phenanthrene (98+%), sodium azide, nitrobenzene (99+%) and 4-Chlorophenol (4-CP, 99+%) were purchased from Sigma–Aldrich Chemical Co. 2,4-Dichlorophenol (DCP, 99.5+%) was purchased from Shanghai Reagent Co. Fuming hydrochloric acid (37%), calcium chloride and anhydrous ethanol (100%) were obtained from Fisher Scientific. Deionized water (DW) was prepared with an Ionpure Plus 150 Service Deionization ion-exchange purification system. All reagents were used as received without further purification. Selected properties of pyrene, phenanthrene, nitrobenzene and DCP are shown in Table S1.

2.2. Synthesis of 1,6-Bis(triethoxysilyl) hexane (BESH)

The modified version of the preparation experiment developed by Oviatt et al. (1993) was used. Briefly, 1,5-hexadiene (13.3 g, 0.162 mol), triethoxysilane (58.66 g, 0.357 mol), 100 mL benzene (99.8%, anhydrous) and 0.10 g chloroplatinic acid were added to a round-bottom three neck flask. The solution was kept in dark for 24 h. The reaction was stirred at room temperature under nitrogen for 3 d. Benzene was removed in vacuo. Distillation (95–105 °C, 0.05 Torr) afforded a clear colorless liquid. The yield was 58%. ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (q, 12 H), 1.40 (m, 4 H), 1.34 (m, 4 H), 1.24 (t, 18 H), 0.66 (m, 4 H).

2.3. Synthesis of biphenyl, phenyl, octane, and hexane BPS

Brij 56 (4 g, 3.56 mmol) was dissolved in 107 mL of 1 M HClaq and 115 mL of deionized water to form a clear Brij 56-HCl-DW mixture solution, which was stirred in a 250 mL round bottom flask equipped with a magnetic stir bar (under nitrogen) for 6 h at 45–55 °C. BESB (8.52 g, 17.8 mmol), BESP (7.17 g, 17.8 mmol), BESO (7.81 g, 17.8 mmol), and BESH (7.3 g, 17.8 mmol) were added dropwise over 2 h to the polymer-containing solution with vigorous stirring, respectively. The four opaque solutions were further stirred for 24 h at 5 °C. The products were filtered, washed three times with deionized water (450 mL) and dried at 23 °C in vacuo. The yields were 57%, 53%, 50%, and 45%, respectively. The template containing one gram sample was extracted with 150 mL of ethanol for 6 h at 50–60 °C. The surfactant (3 g, 2.67 mmol) was removed and the yields were 39.3%, 35.7%, 32.5%, and 28.6%, respectively.

2.4. Characterization of biphenyl, phenyl, octane, and hexane BPS

Fourier transform infrared spectroscopy (FTIR), small angle X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET)-N_2 sorption, ^1H nuclear magnetic resonance (NMR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques were used for characterization. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of four BPS were determined by Thermo Nicolet Avatar 370 Fourier Transform Infrared Spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Philips X'pert instrument using monochromatic Cu Kα radiation ($\lambda = 1.5418$ Å). TEM images were obtained using a Hitachi H-8100 instrument operated at an accelerating voltage of 200 kV. The TEM has high brightness LaB6 electron source and large specimen-tilt (>30°) capabilities. It offers phase contrast resolution of better than 0.26 (point) and 0.14 nm (line). The sample was sonicated for 60 min in an adequate quantity of ethanol and the solution was dropped onto a porous carbon film on a copper grid and then dried before measurement. The SEM was performed using a LEO 1530 Gemini instrument equipped with a field emission cathode with a lateral resolution of 2 nm. The acceleration voltage was chosen between 0.5 and 3 kV. Nitrogen adsorption–desorption isotherm was measured on a Quantachrome Instrument Corporation Autosorb-1 analyzer. The samples were degassed at 200 °C using vacuum below 20 mmHg. The BET (Brunauer–Emmet–Teller) specific surface areas were calculated from the adsorption data in the relative pressure range from 0.05 to 0.235 (Table S2). The Barrett–Joyner–Halenda method was used for calculations of pore diameter and pore volume (Barrett et al., 1951) (Table S2). A new Bruker 300 MHz instrument was used for NMR measurements. ^1H NMR spectra were collected on a Bruker 300 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm and referenced with the internal tetramethylsilane