

Advanced mesoporous organosilica material containing microporous β -cyclodextrins for the removal of humic acid from water

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Abstract

A new mesoporous organosilica material (β -CD-Silica-4%) containing microporous β -cyclodextrins (β -CDs) has been prepared by the co-polymerization of a silylated β -CD monomer with tetraethoxysilane in the presence of a structure-directing template, cetyltrimethylammonium bromide. Solid-state ^{13}C and ^{29}Si NMR studies provided evidence for the presence of covalently attached β -CDs in the mesoporous material. Nitrogen adsorption experiments showed that β -CD-Silica-4% material had a BET surface area of $460\text{ m}^2/\text{g}$ and an average mesopore diameter of 2.52 nm. Small-angle powder X-ray diffraction pattern of β -CD-Silica-4% material revealed the lack of highly ordered mesoporous structure. Adsorption experiments showed that β -CD-Silica-4% material removed up to 99% of humic acid from an aqueous solution containing 50 ppm of humic acid at a solution-to-solid ratio of 100 ml/g.

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1. Introduction

The synthesis of porous materials with tailored properties is one of the most attractive areas of materials science [1–5]. In 1992, the first mesoporous silica material with regular pore channels in the range of 20–100 Å was reported [6,7]. Since then, the synthesis of mesoporous inorganic materials using a structure-directing template has attracted wide attention [8]. Recently, a new generation of mesoporous hybrid silicas containing organic groups on the surfaces of ordered mesoporous silicas was developed by grafting or anchoring of organic guests onto the mesopore channel surface [9–12] or by the direct incorporation of organic groups through co-condensation of organotrialkoxysilanes with tetraalkoxysilanes ($\text{Si}(\text{OEt})_4$ or $\text{Si}(\text{OMe})_4$) [13–19]. This new family of hybrid mesoporous materials is of great interest in environmental remediation and chromatographic separation due to the presence of high surface areas and organic functional groups. Most recently, mesoporous hybrid silica materials with covalently bound specific large organic cavities have been reported [20–23].

Humic acids, which are soluble in alkaline to weakly acidic aqueous solutions, are derived from the degradation of plants and micro-organisms. They represent a broad range of structurally complex compounds containing aliphatic, aromatic, and hydrophilic functional groups, such as carboxyl and phenolic groups. Since humic acids are a well-established cause of color in all open water sources and are also implicated in the formation of disinfection by-products upon chlorination, with potential health implications, their removal is an important task to improve the water quality. Because of the huge volumes involved, effective purification methods for the removal of humic acids from water supplies have to be efficient, fast and inexpensive. Recently, Wirth and Hearn [24] have reported the use of porous zirconia and silica particles modified with anion-exchange functionalities for the removal of humic acid from surface water.

Cyclodextrins (CD) are cyclic oligomers of glucoses, which possess a hydrophilic exterior and a hydrophobic interior into which a variety of hydrophobic organic molecules may be introduced. The CD molecule not only offers a hydrophobic cavity on the nanometer scale, generally smaller than the zeolitic cavities, but also possesses hydrophilic hydroxyl groups outside the cavity, which contribute to the solubility of CD in water. In recent years, β -CDs have

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been immobilized to silica gel via a carbamate spacer, and have been used as a chiral-recognizing perphenylated β -CD column [25,26]. Most recently, the use of mesoporous silica containing immobilized β -CD in chiral separations has been reported by Gallis et al. [27]. We have previously reported the synthesis of ordered mesoporous organosilicas with covalently bound β -CDs in the silica wall [22]. However, more than 14 OH groups in the β -CD units of those materials were converted into $O(CH_2)_3$ groups. Thus, the hydrophilicity of the β -CD units in the β -CD-based materials is much weaker than that of the original β -CD molecules.

In the present work, we report the synthesis of a new type of mesoporous hybrid silica adsorbent containing covalently bound microporous β -CDs for the efficient removal of humic acid contaminant from water. There are two main differences between this new β -CD-based mesoporous organosilica material and our previous β -CD-based mesoporous materials [22]. One is that the β -CD units in this new material are viewed as terminal groups inside the mesopores, whereas the β -CD units in our previous materials [22] function as the bridge groups in the silica walls. The other difference is that the β -CD units in the new material have much more free OH groups than those in our previous materials [22], which may play an important role for their interaction with humic acids that contain a variety of hydrophilic and hydrophobic functional groups. The new β -CD-based mesoporous organosilica material possesses both the advantages of the mesoporous silica, including high surface area and controlled pore size, and the advantages of β -CD hosts, such as their ability to incorporate hydrophobic organic molecules into their hydrophobic cavities and their ability to form hydrogen bonding with hydrophilic compounds through their OH groups. Based on these characteristics, we expect that this new material would have fast sorption kinetics for humic acids.

2. Experimental

2.1. Materials

Most of the solvents and all reagents were obtained from commercial supplies and used without further purification. THF and DMF employed in the syntheses were dried over 3 Å molecular sieves. Cycloheptaamylose (β -CD) was obtained from Aldrich Chemical Co. Inc., purified by recrystallization from water three times, and dried at 110 °C for 12 h. 3-Isocyanatopropyltriethoxysilane was obtained from Gelest Inc. and used without purification. Tetraethoxysilane (TEOS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich Chemical Corp. and used without further purification. Humic acids were obtained from Alfa Aesar and Fisher Scientific, respectively.

2.2. Characterization of materials

FTIR spectra were recorded from KBr pellets using a Galaxy Series FTIR 5000 spectrophotometer. Liquid state 1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400.2 MHz (1H) and 100.6 MHz (^{13}C). Liquid state ^{29}Si NMR spectra were recorded on a Varian Chemagnetics Infinity Plus 500 spectrometer operating at 99.3 MHz. High-resolution ^{13}C and ^{29}Si MAS NMR spectra were run at 75.5 and 59.6 MHz, respectively, on a Varian VXR300 spectrometer with a ZrO_2 rotor and two aurum caps. The spinning speed ranged between 3 and 4 kHz. The experiments were made using a high-power proton decoupling (DD). The XRD patterns were obtained with a Rigaku DMAX-B diffractometer using $Cu K\alpha$ radiation. Nitrogen sorption isotherms of the materials were taken at 77 K by using nitrogen in a conventional volumetric technique by an Autosorb-1 volumetric sorption analyzer controlled by Autosorb-1 for windows 1.19 software (Quantachrome). All samples were outgassed at 80 °C until the test of outgas pressure rise was passed by 5 μ Hg/min prior to their analysis. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P_0) range 0.1–0.3. TEM images were recorded on a Hitachi HF-2000 transmission electron microscopy. UV-Vis spectra were recorded at 25 °C with an Agilent 8453 UV-Vis spectrophotometer.

2.3. Synthesis of CD-based monomer 1

To a stirred solution of purified β -CD (5.74 g, 5.0 mmol) in 70 ml of dried DMF, was added 3.70 g (15.0 mmol) of 3-isocyanatopropyltriethoxysilane. The solution was stirred at 70 °C under nitrogen for 24 h. The solvent was removed under reduced pressure under nitrogen. The product monomer **1** was obtained as a light yellow solid. Yield 97%. IR (KBr) 3390 (N–H), 1713 (C=O), 1542 (NH–CO). 1H NMR (DMSO) δ 0.52 (m, 6H, $SiCH_2$), 1.15 (t, 27H, $SiOCH_2CH_3$), 1.44 (m, 6H, $SiCH_2CH_2$), 3.27 (m, $SiCH_2CH_2CH_2$), 2.87–3.73, 4.19–4.88, 5.58–5.77 (m, 67H, $SiOCH_2$, H1, H2, H3, H4, H5). ^{13}C NMR (DMSO) δ 7.3, 18.3, 23.0, 43.3, 57.8, 60.0, 69.8, 72.2, 73.0, 81.6, 101.6, 102.0, 155.8. ^{29}Si NMR (DMSO) δ –46.2.

2.4. Preparation of as-synthesized organosilica materials (β -CD-Silica-X%-S)

A mixture of monomer **1** dissolved in DMF and TEOS corresponding to the appropriate mole fraction, with a total of 32.5 mmol Si (for example, 6.01 g (28.6 mmol) of TEOS and 2.44 g (1.3 mmol) of monomer **1** for sample β -CD-Silica-4%-S), was added slowly to the base-surfactant solution with gentle stirring. The base-surfactant solution was prepared by adding 1.10 g of CTABr (3.0 mmol) to a

solution of NaOH (0.71 g, 18 mmol) and deionized water (58.5 g, 3.3 mol), and stirring at 40 °C for 30 min in a closed flask. The mixture was then heated at 100 °C for 24 h. The white solid was collected by filtration, washed thoroughly with water, acetone, THF and diethyl ether, and air-dried under ambient conditions. A mole ratio of 1.00 TEOS:z monomer **1**:130 H₂O:0.7 NaOH:0.12 CTAB was used during the synthesis. Samples were prepared with monomer **1** to the total amount of Si molar ratios ($z/(1 + 3z)$) of 0/100 (β -CD-Silica-0%-S), 4/100 (β -CD-Silica-4%-S), 10/100 (β -CD-Silica-10%-S).

2.5. Surfactant extraction

The surfactant template was removed from the as-synthesized organosilica β -CD-Silica-X%-S materials through solvent extraction. An as-synthesized sample (5 g) was refluxed in ethanol–HCl (100:1) for 24 h. The powder was filtered, washed with methanol, and air-dried at room temperature to provide the surfactant-extracted β -CD-based β -CD-Silica-X% material.

2.6. Adsorption of humic acid by the surfactant-extracted β -CD-Silica-X% materials

β -CD-Silica-X% (100 mg) was stirred with 10 ml of aqueous solution containing humic acid (Fisher Scientific or Alfa Aesar, 50 ppm) at 25 °C for 18 h. The suspension was filtered, and the residual humic acid concentration in the filtrate was measured using UV-Vis spectroscopy. The UV spectrum of the humic acid aqueous solution showed a shoulder between 250 and 350 nm representing the aromatic components of the humic acid. The absorbance changes at 275 nm wavelength of the humic acid solution before and after the adsorption by β -CD-Silica-X% were used to monitor the adsorption of humic acid to β -CD-Silica-X% material. The amount of humic acid adsorbed by β -CD-Silica-X% was then determined by subtracting the humic acid in the filtrate from that of the untreated humic acid solution. The same procedure was used with variation of adsorption time, concentration of humic acid, type of humic acid, and the amount of solid material.

2.7. Regeneration of humic acid-loaded β -CD-Silica-4%

Two hundred milligrams of β -CD-Silica-4% material loaded with a known amount of humic acid (Fisher Scientific) was shaken in 20 ml of a concentrated sodium chloride aqueous solution (brine, pH 7.72) at 25 °C for 6 h. The suspension was filtered, and the concentration of humic acid in the filtrate was measured by UV-Vis spectroscopy. The amount of humic acid removed from β -CD-Silica-4% material then was determined by difference.

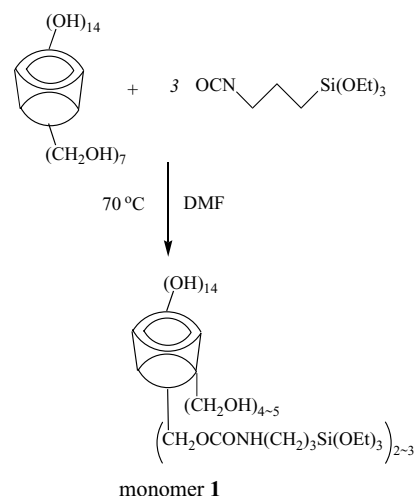


Fig. 1. Synthesis of β -CD-based monomer **1**.

3. Results and discussion

3.1. Synthesis

The strategy to link β -CD hosts to mesoporous silica framework involved covalently attaching two to three triethoxysilyl groups to β -CD through carbamate linkages (Fig. 1), and co-polymerizing the resulting β -CD-based monomer **1** with TEOS in the presence of a structure-directing surfactant, cetyltrimethylammonium bromide (CTAB), to produce the β -CD-based organosilicas (Fig. 2). In the present study, we have identified the surfactant-templated mesoporous silicas as platform substrates for preparing β -CD-based mesoporous organosilica materials. The basis of this approach was to couple the use of supramolecular surfactant template with co-condensation reactions involving siloxane (TEOS) and β -CD-based

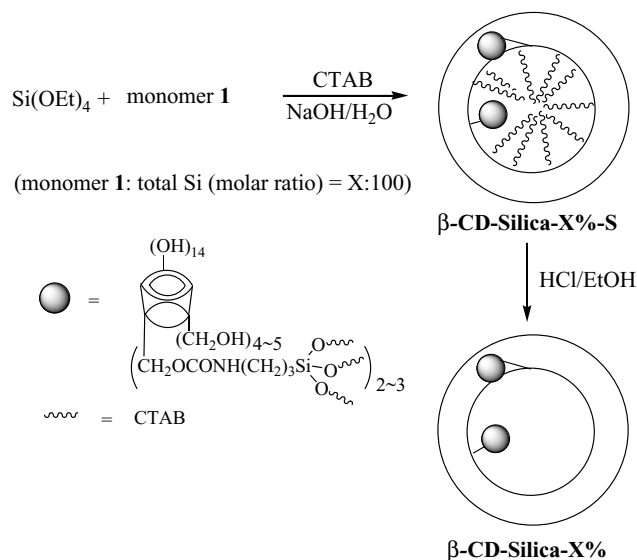


Fig. 2. Preparation of β -CD-Silica-X% materials.

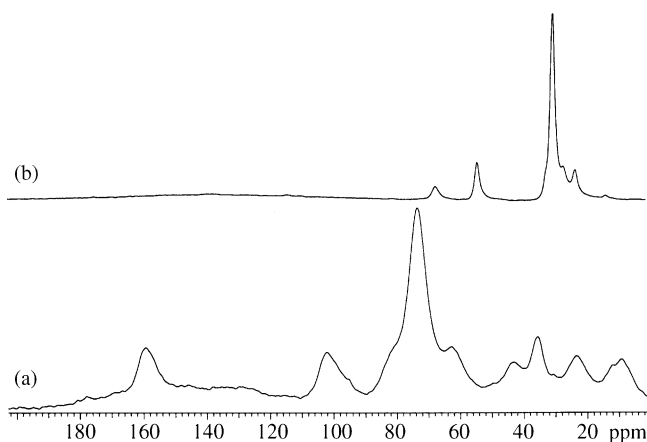


Fig. 3. ^{13}C NMR spectra of (a) β -CD-Silica-4% material, and (b) CTAB surfactant.

monomer 1. TEOS was used as the primary silica source and as a reagent for the formation of fully saturated linkages that are required to maintain structural integrity in the organo-silica-surfactant mesophase. The surfactant was removed by treatment with ethanol containing aqueous hydrochloric acid to produce the mesoporous organosilicas.

The as-synthesized materials were named β -CD-Silica-X%-S and the surfactant-extracted materials were named β -CD-Silica-X%. β -CD-Silica-0%-S and its extraction product β -CD-Silica-0% were prepared entirely from TEOS and contain no β -CD host molecule.

3.2. Characterization

3.2.1. NMR characterization

The chemical structure of the mesoporous β -CD-Silica-X% materials was studied with solid-state NMR. The carbon spectrum of β -CD-Silica-4% is shown in Fig. 3a. The carbon in the urethane connector (OCONH) is found in δ 159, and the carbons in the β -CD unit are found in the region δ 60–110, indicating that the covalently bound β -CD units are intact during the template-directed sol-gel process. The carbons in the carbamate connector (OCONHCH₂CH₂CH₂Si) are found in the region δ 9–50. Compared with the solid-state carbon NMR spectrum of CTAB surfactant (Fig. 3b), the carbon spectrum of β -CD-Silica-4% lacks all carbon resonances from CTAB, indicating the complete removal of the surfactant from the as-synthesized β -CD-Silica-4%-S by solvent extraction. The solid-state ^{29}Si NMR spectrum of β -CD-Silica-4% sample (Fig. 4) shows two signals at δ -62.1 and -65.4 attributed to T² (CSi(OH)O₂) and T³ (CSiO₃) substructures, respectively, as well as one strong signal at δ -110.8 attributed to Q⁴ (SiO₄) substructure.

3.2.2. Surface area

The nitrogen adsorption isotherm of β -CD-Silica-0% (Fig. 5a) exhibits a type IV isotherm, indicating that the

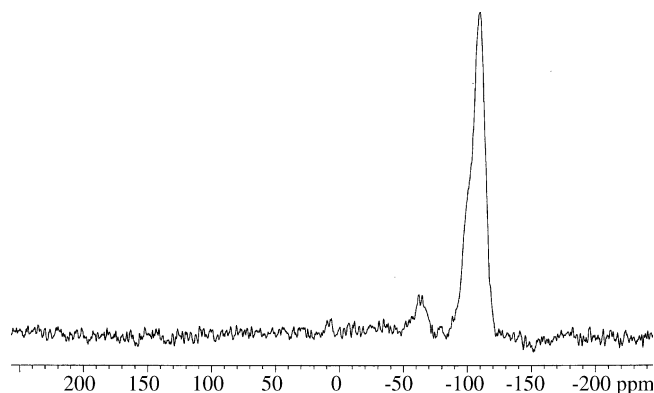


Fig. 4. Solid state ^{29}Si NMR spectrum of β -CD-Silica-4% material.

pore size is in the mesopore range. The steep slope at low relative pressure in the nitrogen adsorption isotherm curve of β -CD-Silica-4% (Fig. 5b) reveals that the isotherm is not strictly of type IV (indicating the mesoporosity) [28], but it indicates that the isotherm has a superposition of type I and type IV isotherms. This superposition indicates the existence of additional β -CD-based micropores in mesoporous β -CD-Silica-4% material. The pore size distribution of β -CD-Silica-4% calculated from the adsorption branch of the nitrogen isotherm (Fig. 5b(inset)) by using the method proposed by Barrett, Joyner, and Halenda [29] (BJH method) shows a bimodal pore size distribution, with 0.69 nm-sized micropores and 2.52 nm mesopores. In contrast, the nitrogen adsorption isotherm of β -CD-Silica-10% (Fig. 5c) is of type II adsorption curve, suggesting that it is nonporous. Table 1 gives the BET surface areas for the β -CD-Silica-X% materials in the third column. The β -CD-Silica-0% and β -CD-Silica-4% have high BET surface areas of 720 and 460 m²/g, respectively.

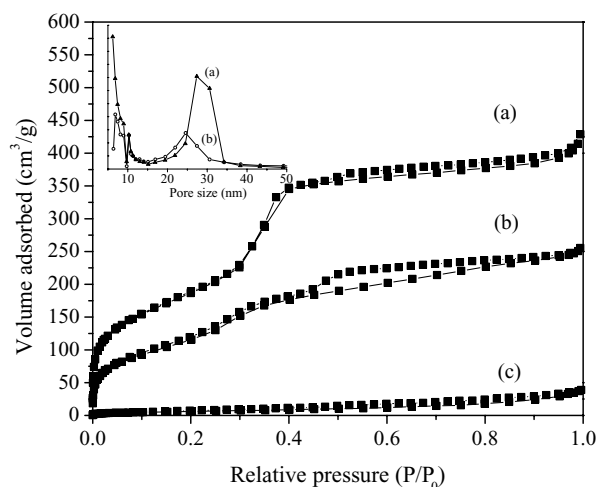


Fig. 5. Nitrogen adsorption-desorption isotherms of (a) β -CD-Silica-0%, and (b) β -CD-Silica-4% and (c) β -CD-Silica-10%.

Table 1
Physical and surface properties of β -CD-based organosilica materials

Material	XRD $d(100)$ (nm)	BET surface area (m ² /g)	Mesopore diameter (nm) ^a
β -CD-Silica-0%	3.40	720	2.79
β -CD-Silica-4%	–	460	2.52
β -CD-Silica-10%	–	24	–

^a Calculated from the adsorption branch by using the BJH method.

3.2.3. Powder X-ray diffraction

Fig. 6 shows the small angle powder XRD patterns of the surfactant-extracted β -CD-Silica-X% materials. The XRD pattern of β -CD-Silica-0% pure silica material (Fig. 6a) shows a single strong and sharp low angle diffraction ($d(100)$) at $2\theta = 2.6^\circ$, corresponding to the presence of highly ordered mesoporous structure. The XRD pattern of β -CD-based β -CD-Silica-4% material (Fig. 6b) reveals the presence of a relatively broad signal at $2\theta = 2.7^\circ$, which is an indication that the β -CD-based β -CD-Silica-4% material does not possess highly ordered mesoporous structure. Table 1 gives the actual $d(100)$ values in the second column. As the proportion of β -CD units increased to 10% (β -CD-Silica-10%), no pronounced diffraction peak appeared in its small angle XRD pattern, indicating that β -CD-based β -CD-Silica-10% material lacks any ordered porous structure.

3.3. Humic acid adsorption properties

Humic acids are a complex family of lignin-derived metabolites containing carboxylic groups with a range of structural features which involve different types of hydrogen bonding and hydrophobic characteristics. To achieve efficient adsorption with humic acids in water, the aforementioned organosilica material β -CD-Silica-4% with microporous β -CD units and mesoporous silica framework

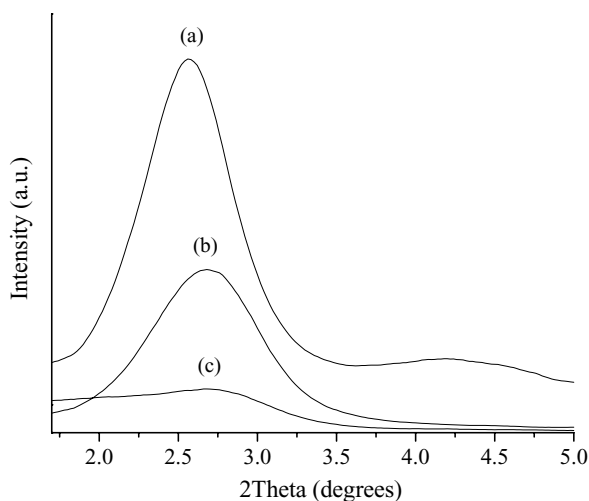


Fig. 6. Powder X-ray diffraction patterns of (a) β -CD-Silica-0%, (b) β -CD-Silica-4%, and (c) β -CD-Silica-10%.

Table 2
Adsorption of different humic acids by β -CD-based organosilica materials from water^a

Material	Humic acid adsorbed (%)	
	A (50 ppm) ^b	B (50 ppm) ^c
β -CD-Silica-0%	49.1	39.0
β -CD-Silica-4%	99.6	99.1
β -CD-Silica-10%	33.0	25.2

^a Experimental conditions: 0.1 g of solid material in 10 ml of aqueous solution, 18 h, 25 °C.

^b Humic acid A is purchased from Fisher Scientific.

^c Humic acid B is purchased from Alfa Aesar.

was selected for this investigation. The β -CD units have both the hydrophobic cavities and hydrophilic exterior. The adsorption behavior of this material was characterized in terms of its apparent adsorption isotherms but it should be noted that these isotherms will reflect only the average behavior of the related compounds within the humic acid mixture rather than the isothermal behavior of an individual member. The humic acids adsorption properties of the β -CD-Silica-0% and β -CD-Silica-10% materials were also studied for comparison purpose. The β -CD-Silica-X% adsorbent was suspended in an aqueous solution of the humic acids (0.1 g adsorbent per 10 ml), and the adsorption of the humic acids was monitored by the absorbance changes at 275 nm in its UV spectrum.

Table 2 summarizes the adsorption of two humic acids from different companies by β -CD-Silica-X% materials. It can be seen from Table 2 that when the humic acid (50 ppm) was treated with these adsorbents, the mesoporous CD-silica-0% pure silica material could adsorb 49.1% of humic acid (Fisher) (or 39.0% from Alfa Aesar). The presence of β -CD units made a mesoporous organosilica adsorbent β -CD-Silica-4% that is superior in its ability to remove humic acid from water (>99.0% for humic acids from both Fisher and Alfa Aesar) to that of mesoporous β -CD-Silica-0% pure silica adsorbent. However, only 33.0% of humic acid (Fisher) (or 25.2% of humic acid from Alfa Aesar) was adsorbed when using the β -CD-based non-porous β -CD-Silica-10% material, which contains much higher number of β -CD units than the β -CD-based mesoporous β -CD-Silica-4% material. These results indicate that the mesoporous structure and the microporous β -CD host are two key factors affecting the adsorption capability of this type of adsorbents.

The treatment of aqueous solutions of humic acids (Alfa Aesar) in relatively high concentrations (100 and 500 ppm, respectively) with mesoporous β -CD-Silica-4% material resulted in 96.7 and 60.7% adsorption, respectively. Because of the structural complexity of the humic acid sample, the loading capacity of this type of adsorbents can only be expressed in terms of mg/g. The apparent loading capacity of β -CD-Silica-4% material was about 30 mg humic acid (Alfa Aesar) per g of adsorbent.

The adsorption kinetics of the β -CD-Silica-4% material for humic acid is dramatically fast. The β -CD-Silica-4% material can reduce a 50 ppm humic acid aqueous solution to less than 1.0 ppm within 1 min and to less than 0.3 ppm within 2 h at a solution-to-solid ratio of 100 ml/g.

If the β -CD-based mesoporous organosilica materials are used for the removal of humic acids from water in industry, ideally they should be renewable. However, we found that the humic acid-loaded β -CD-Silica-4% material can be partially regenerated chemically. The treatment of 0.2 g of humic acid-loaded β -CD-Silica-4% material with 20 ml of a concentrated NaCl solution (brine) for 6 h resulted in only 30% removal of the loaded humic acid. Further exploration of new effective regeneration methods for the humic acid-loaded β -CD-Silica-4% material is still in progress.

4. Conclusions

Mesoporous β -CD-containing organosilica material possessing high capability to adsorb humic acid contaminants from water was synthesized by co-polymerization of tetraethoxysilane and the silylated β -CD monomer in the presence of a surfactant as the template. Surfactant extraction resulted in an insoluble mesoporous organosilica material containing covalently bound microporous β -CD moieties. Spectroscopic characterization provided evidence for retention of the covalently attached β -CD hosts and complete removal of the surfactant. Powder XRD and nitrogen adsorption studies demonstrated that the β -CD-containing organosilica material possesses a mesoporous structure and a high BET surface area. Adsorption experiments have shown that the mesoporous β -CD-containing organosilica material can remove two different types of humic acids from water in high efficiency. This new material is potentially useful for a wide variety of applications in environmental remediation and chromatographic separation.

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