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β-Cyclodextrin functionalized polystyrene porous monoliths for separating phenol from wastewater

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ABSTRACT

A β-cyclodextrin (β-CD) functionalized polystyrene porous monolith was prepared by the following procedure: First, β-CD was modified with allyl bromide leading to allyl-β-cyclodextrin (allyl-β-CD); then a concentrated emulsion was prepared using a mixture of allyl-β-CD, styrene, and divinyl benzene as the continuous phase and water as the dispersed phase. In the third step, a β-cyclodextrin (β-CD) functionalized polystyrene porous monolith was obtained by copolymerization of allyl-β-CD and styrene followed by removal of the water phase. Since the allyl-β-CD contained both hydrophilic and hydrophobic groups, it tended to move towards the water/oil interface. As a result, the internal surfaces of the porous monolith were enriched with β-CD. This enrichment was indicated by X-ray photoelectron spectroscopy characterization. The high content of β-CD and the high specific surface area of the porous monolith both contributed to a high adsorption capacity. For example, the maximum adsorption of phenol was 5.74 mg/g. Importantly, the porous monolith could be easily regenerated and recycled through desorption with ethanol and it was found that the adsorption properties remained stable for at least five adsorption/desorption cycles.

1. Introduction

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide consisting of seven glucose units connected through α-(1,4) linkages. It is topologically represented as a toroid with primary hydroxyl groups located on the lower face secondary hydroxyl groups on the upper face (Rekharsky & Inoue, 1998; Szejtli, 1998; Van de Manakker, Vermonden, van Nostrum, & Hennink, 2009), and it forms strong host–guest complexes with hydrophobic molecules residing inside the torroid. Consequently it has found applications in foodstuffs, pharmaceutical manufacture, drug delivery, chemical industries, agriculture and environmental engineering (Hergert & Escandar, 2003; Prabaharan & Gong, 2008; Hedges, 1998; Yilmaz, Memon, & Yilmaz, 2010). Here, to develop a material suitable for wastewater remediation, we take advantage of the ability of β-CDs to sequester moderately hydrophobic organic compounds, such as phenol (Bibby & Mercier, 2003; Chen et al., 2006), chlorophenol (Schofield, Bain, & Badyal, 2012), benzoic acid (Chai & Ji, 2012), and heavy metals (Badruddoza, Shawon, Tay, Hidajat, & Uddin, 2013). In this report, in order to recover and regenerate, we overcome the previously reported difficulties associated with β-CD use in wastewater treatment by fixing the β-CD to a water insoluble support (Del Valle, 2004).

In recent years, many studies have been carried out on the fabrication of cross-linked β-cyclodextrin polymers for the adsorption of phenol (Romo, Penas, Isasi, Garcia-Zubiri, & Gonzalez-Gaitano, 2008; Yamasaki, Makihata, & Fukunaga, 2006). The chemical stability of polystyrene makes it a good support material for β-CD and Jiang et al. (2006) prepared a novel copolymer via copolymerization of (6-O-butene diacid ester)-β-cyclodextrin and styrene. This material exhibited a strong affinity towards phenol. Sun et al. (2010) prepared a novel β-CD containing an insoluble bimodal porous polymeric material that adsorbed aromatic amine compounds. However, in these reports, the lack of sufficient functional groups for phenol removal and diffusion limitations within the

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support matrix have led to a decrease the adsorption efficiency (Yamasaki, Makihata, & Fukunaga, 2008).

In order to maximize the contact interface between wastewater and the absorbent, porous materials, especially porous polymers are the best choice. They have the attributes of high specific surface area and plenty of surface functional groups. Porous polymers have been widely applied as chromatographic media (Rolison, 2003), in the catalysis of chemical and biochemical reactions (Zou, Huang, Ye, & Luo, 2002), and adsorption process (Yang, Wei, Wang, & Tong, 2013). Among various methods to prepare porous polymeric materials, that using a concentrated emulsion as a polymerization template (Pulko & Krajnc, 2012; Han, Du, Zou, Li, & Zhang, 2014) constitutes a flexible and easily controlled approach. Such open cell structures readily promote the diffusion of trace contaminants such as phenol into the porous polymer materials.

In this paper, β-CD functionalized polystyrene porous monoliths with an open cell structure and a high β-CD content were prepared by concentrated emulsion polymerization. To do this, first β-CD was modified with allyl bromide to introduce vinyl groups that could copolymerize with styrene monomers. A concentrated emulsion was then formed using this allyl-β-CD, styrene, and divinyl benzene as the continuous phase and water as the dispersed phase. By having a high volume fraction for the dispersed phase (>74%), the continuous phase was in fact a thin film surrounding the dispersed droplets. An important feature of this preparation method is that the remaining hydroxyl groups on the allyl-β-CD drag the allyl-β-CD towards the water/oil interface. This results in the W/O (water/oil) interfaces being enriched with allyl-β-CD. Following initiation, the monomers in the continuous phase undergo a copolymerization reaction, resulting in the generation of a porous polymer monolith. This monolith possesses a high specific surface area and has an abundance of active β-CD on the exposed internal surfaces (where the W/O interfaces were). This material is then readily able to absorb materials such as phenol from wastewater.

2. Experimental

2.1. Materials

β-Cyclodextrin (β-CD), allyl bromide, and divinyl benzene (DVB) were supplied by Aladdin Chemical Company. Styrene, phenol, p-chlorophenol and 2,4,6-trichlorophenol were supplied by Chemical Factory of Tianjin. Sodium hydroxide, N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate, potassium persulfate, potassium sulfate, and anhydrous ethanol were purchased from Beijing Chemical Works. Sorbitan monooleate (Span 80) were provided by Xilong Chemical Co., Ltd.

2.2. Preparation of allyl-β-cyclodextrin (allyl-β-CD)

The preparation of allyl-β-CD was carried out according to the method described previously with some modifications (Eskandani, Huin, & Guégan, 2011). A mixture of β-CD (2.3 g) and NaOH (8.96 g) was dissolved in a 100 mL 50:50 mixture of DMF and DMSO. Allyl bromide was then added (0–40% w/w) with vigorous stirring. The reaction was kept for 48 h at 5 °C. The product was precipitated by deionized water, then extracted with ethyl acetate, and finally obtained by vacuum rotary evaporation.

2.3. Preparation of β-CD functionalized polystyrene porous monolith

A typical preparation of concentrated emulsion was as follows: the organic phase contained allyl-β-CD, styrene, DVB (0.75 g) and Span 80 (1.0 g) was mixed in a round-bottom flask equipped with an overhead leaf-shaped stirrer paddle at 600 rpm. Then the aqueous phase consisting of initiator $K_2S_2O_8$ (0.075 g) and electrolyte K_2SO_4 (0.188 g) in deionized water (45 g) was introduced dropwise into the organic phase with vigorous stirring, and a milky emulsion was obtained. The concentrated emulsion was stood for a certain time at room temperature, and then copolymerized at a certain temperature as detailed in Section 3, for 24 h. The product was washed by deionized water and ethanol, and dried in vacuum at 60 °C for 48 h.

2.4. Characterization

FT-IR spectra was recorded on a Nicolet 750 spectrophotometer (Thermo Fisher Nicolet, Orlando, FL). ^{1}H NMR (Bruker, AV600) was used to characterize the chemical structure of the product. The surface composition of the porous materials was determined using X-ray photoelectron spectroscopy (XPS, ESCALAB 250X). Scanning electron microscopy (SEM, S3700, Hitachi Ltd., Tokyo, Japan) and the Brunauer–Emmet–Teller (BET) method were used to measure the morphology of porous monoliths.

2.5. Adsorption/desorption experiments

In a typical adsorption procedure, all batch experiments were carried out by putting 100 mL of solution with a known adsorbate concentration (200 mg/L) into chromatography column which was filled with 0.5 g of dry β-CD adsorbents at 25 °C. The adsorption equilibrium, q_e (mg/g), was calculated according to

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e were the initial and equilibrium concentrations (mg/L), V was the volume (L) of the solution used in the adsorption experiment, and W was the weight (g) of adsorbent. Data was representative of at least three experiments, and the standard deviations were less than 3.0%. The residual adsorbate concentration in solution was determined by UV spectrophotometer (Hitachi U-3010) at 270 nm for phenol, 280 nm for p-chlorophenol and 286 nm for 2,4,6-trichlorophenol (Bosch, Font, & Mañes, 1987; Zhou et al., 2014). The standard curve was obtained by preparing standard solution with different concentrations of solution (0, 25, 50, 75, 100, 150, 200 mg/L). Each experiment was done three times under identical conditions.

Desorption and regeneration behaviour of β-CD functionalized polystyrene porous monolith was evaluated. The column was washed with anhydrous ethanol to remove adsorbate from the adsorbent. Then the adsorbent was thoroughly washed with deionized water and used again in an adsorption experiment. The adsorption–desorption process was repeated five times, and the amount of adsorbate was calculated according to Eq. (1).

3. Results and discussion

3.1. ^{1}H NMR analysis of allyl-β-CD

^{1}H NMR analysis results of pure β-CD and allyl-β-CD were shown in Fig. 1. Compared with the spectrum of pure β-CD (Fig. 1a), new proton peaks are seen at 4.1 ppm (H_7), 5.8–6.02 ppm (H_8), and 5.1–5.3 ppm (H_9) in Fig. 1b. These represent the allyl groups of allyl-β-CD (Schneider, Hacket, Rüdiger, & Ikeda, 1998). According to the integration areas the average degree of substitution was 6.5 allyl groups per β-CD toroid. Thus, a well functionalized allyl-β-CD was synthesized successfully.