Carbohydrate Polymers 120 (2015) 85–91

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

Jiaxi Han, Kaijun Xie, Zhongjie Du, Wei Zou, Chen Zhang*

Key Laboratory of Carbon Fiber and Functional Polymers (Beijing University of chemical Technology), Ministry of Education, College of Materials Science and Engineering, Beijing University of chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 9 December 2014
Accepted 14 December 2014
Available online 22 December 2014

Chemical compounds studied in this article:
β-Cyclodextrin (PubChem CID: 444041)
Allyl bromide (PubChem CID: 7841)
Divinyl benzene (PubChem CID: 66041)
Styrene (PubChem CID: 7501)
Phenol (PubChem CID: 996)
p-Chlorophenol (PubChem CID: 4684)
2,4,6-Trichlorophenol (PubChem CID: 6914)

Keywords:
β-Cyclodextrin
Concentrated emulsion polymerization
Adsorption
Phenol
Porous

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

* Corresponding author. Tel.: +86 10 64428804; fax: +86 10 64428804.
E-mail address: zhangch@mail.buct.edu.cn (C. Zhang).

http://dx.doi.org/10.1016/j.carbpol.2014.12.011
0144-8617/

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.

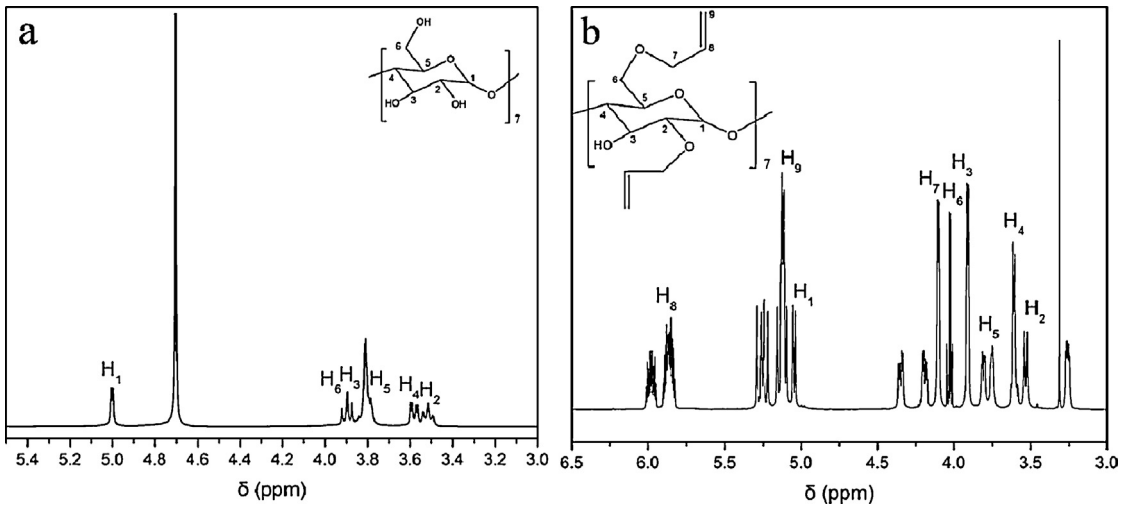

Fig. 1. ^{1}H NMR spectra of (a) β-CD and (b) allyl-β-CD in d^{6}-DMSO.

3.2. Characterization of β-CD functionalized polystyrene porous monolith

Fig. 2 shows the FTIR spectra of polystyrene (trace a) and a β-CD functionalized porous monolith (trace b). In trace b, a new characteristic peak for C—O—C at 1033 cm^{-1} was observed in addition to the regular polystyrene peaks. This indicates the occurrence of copolymerization between allyl-β-CD and styrene.

Fig. 3 compares the XPS spectra for polystyrene (trace a) and the monolith sample (trace b). The emission peak at 526.95 eV for oxygen element in Fig. 3b indicates the existence of β-CD groups. The content of oxygen element in the surface of monolith was estimated at 16.66 wt %, which indicates that a large number of allyl-β-CD moieties can be found at the interface of the β-CD functionalized polystyrene porous monolith (the oxygen content of pure β-CD is ~49 wt%).

The morphology of the porous monolith is shown in the SEM images (Fig. 4). It was observed that increasing the allyl-β-CD content leads to an incease in the distribution of pore sizes and a decrease in the average pore size. Furthermore, from BET results (Table 1), it was clear that the specific surface area and the pore volume decreased sharply when going from 0 wt% to 15 wt% allyl-β-CD in the preparation solution. This is because the allyl-β-CD hydrophilicity is harmful to the stability of concentrated emulsion. However, as the content of allyl-β-CD is increased above this level, the specific surface area and the pore volume changes only moderately. As a result, the open cell structure and a reasonable specific surface area of the monolith are always obtained, even for high contents of allyl-β-CD. Importantly, as shown below, the β-CD groups in all of these structures provide sufficient sites for effective phenol adsorption.

Table 1
BET characterization of β-CD functionalized polystyrene porous monolith.

Content of allyl-β-CD (wt%)	Specific surface area (m^2/g)	Pore volume (cm^3/g)
None	21.197	0.151
15	11.961	0.036
27	11.960	0.039
40	11.607	0.034

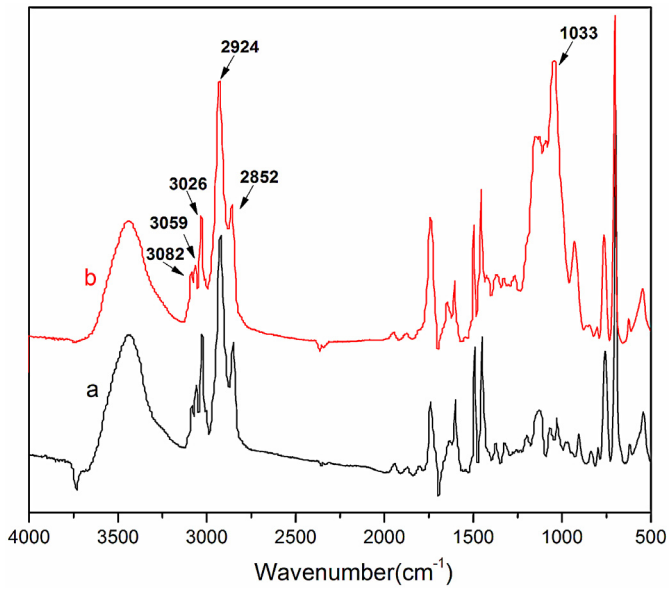

Fig. 2. FT-IR spectra of (a) porous polystyrene and (b) β-CD functionalized polystyrene porous monolith.

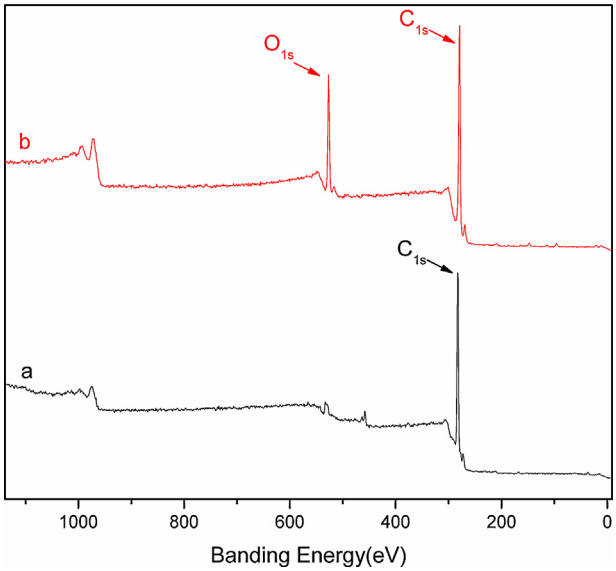

Fig. 3. Typical XPS scans of the surface of (a) polystyrene porous monolith and (b) β-CD functionalized polystyrene porous monolith.

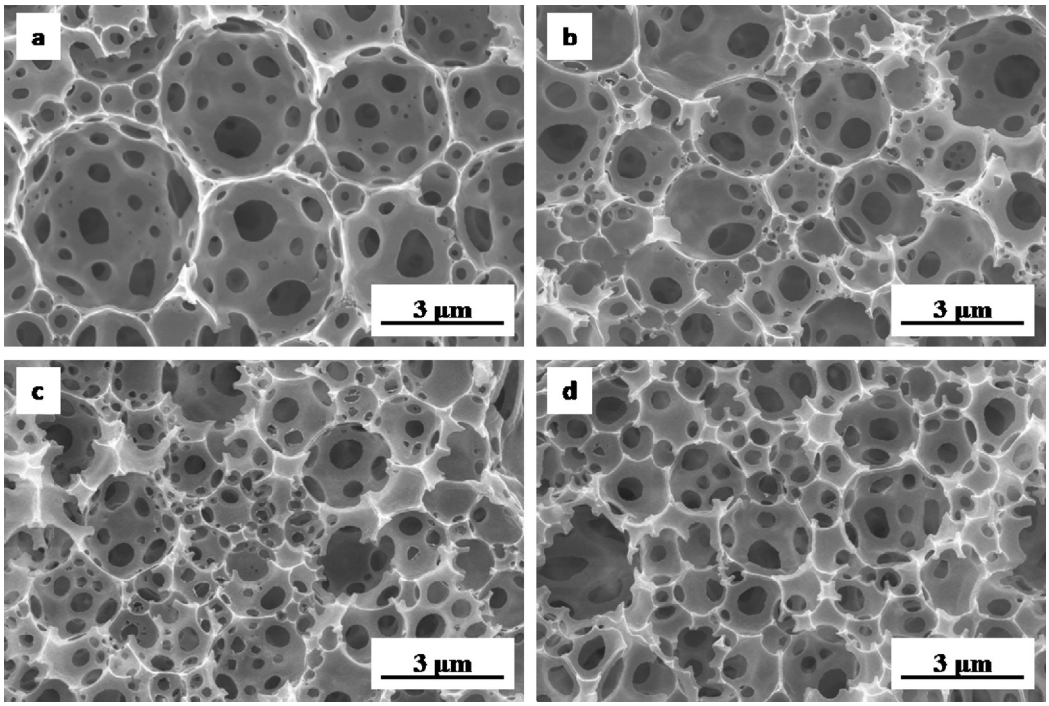

Fig. 4. SEM images of β-CD functionalized polystyrene porous monolith with different allyl-β-CD content ((a) 0 wt%; (b) 15 wt%; (c) 27 wt%; (d) 40 wt %).

3.3. Effect of volume fraction and allyl-β-CD content on adsorption process

The porous monoliths were prepared from concentrated emulsions with different volume fractions of the dispersed (water) phase (ϕ), ranging from 80% to 95%. It was found that the adsorption capacity of the monolith increased with increasing ϕ until ϕ equaled 95%, as shown Fig. 5a. The reason was simple, the higher ϕ, the larger the specific surface area of the porous monolith, and the higher the adsorption capacity. However, at a level of ϕ equal to 95%, the concentrated emulsion became unstable. This resulted in a low specific surface area and significant decrease in the adsorption capacity.

The allyl-β-CD concentration in the continuous phase of the concentrated emulsion also influences the adsorption capacity, as shown in Fig. 5b. To study this effect, the volume fraction of the concentrated emulsion was kept at 90% and the polymerization temperature used was 65 °C whilst the allyl-β-CD concentration was varied. Initially, the adsorption capacity increased with increasing content of allyl-β-CD until 27 wt% (adsorption capacity 3.56 mg/g). Since each allyl-β-CD group contributes to the system's active sites for phenol adsorption, the higher the allyl-β-CD content would be expected to lead to a higher adsorption capacity. Unfortunately, as indicated above, too high a content of allyl-β-CD in the preparation solution impairs the stability of the concentrated emulsion resulting in a decrease in the specific surface area and a lower adsorption capacity. It was found that 27 wt% constituted the optimal allyl-β-CD content for phenol adsorption in this work.

3.4. Migration of allyl-β-CD to the interface of β-CD functionalized polystyrene porous monolith

As indicated above, each allyl-β-CD molecule has several hydrophilic hydroxyl groups. When the concentrated emulsion is left to stand, these hydroxyl groups cause the molecule to migrate to the vicinity of the water/oil interface (Fig. 6c). This migration of allyl-β-CD in the formed monoliths was evaluated by measuring both the surface oxygen content (according to XPS) and the adsorption capacities. Changes in these two characteristics parallel each other, as shown in Fig. 6. In Fig. 6a, the higher oxygen content corresponds to a high concentration of allyl-β-CD on the surface, therefore, a higher adsorption capacity. With an increase in standing time, the more allyl-β-CD accumulates on the W/O interface, resulting in higher adsorption capacities being seen. Fig. 6a indicates that an adsorption capacity of 5.5 mg/g was obtained when the standing time was 8 h. However, if the standing time was too long, some of the allyl-β-CD partitions into the aqueous dispersed phase, and thus does not participate in the polymerization reaction. These monoliths have low adsorption capacities.

The migration of allyl-β-CD was also influenced by the polymerization temperature. Here there are two competing effects: When the polymerization temperature is low, the viscosity of the system is high, and migration of the allyl-β-CD is slow. In other hand, the use of low temperatures delays the gel point, leading to longer migration times before the monolith is fully formed. It was observed that the surface oxygen content and adsorption capacity increased with increasing polymerization temperature. However, at the higher temperatures used, allyl-β-CD can also become a cross-linker in the polymerization leading to a reduction in the migration of allyl-β-CD. As shown in Fig. 6b, the oxygen content and adsorption capacity started to decrease above 60 °C. It was thus demonstrated that the polymerization temperature is an important factor influencing migration of allyl-β-CD to the W/O interface.

3.5. Adsorption–desorption behaviour of β-CD functionalized polystyrene porous monolith

As with many compounds and materials, the adsorption capacity is affected by adsorption environment, e.g. the pH of the solution (water) in which the adsorbant is immersed. Fig. 7a shows the effect of pH on phenol adsorption. When the pH was below 4.0, the adsorption capacity increased gradually with increasing pH

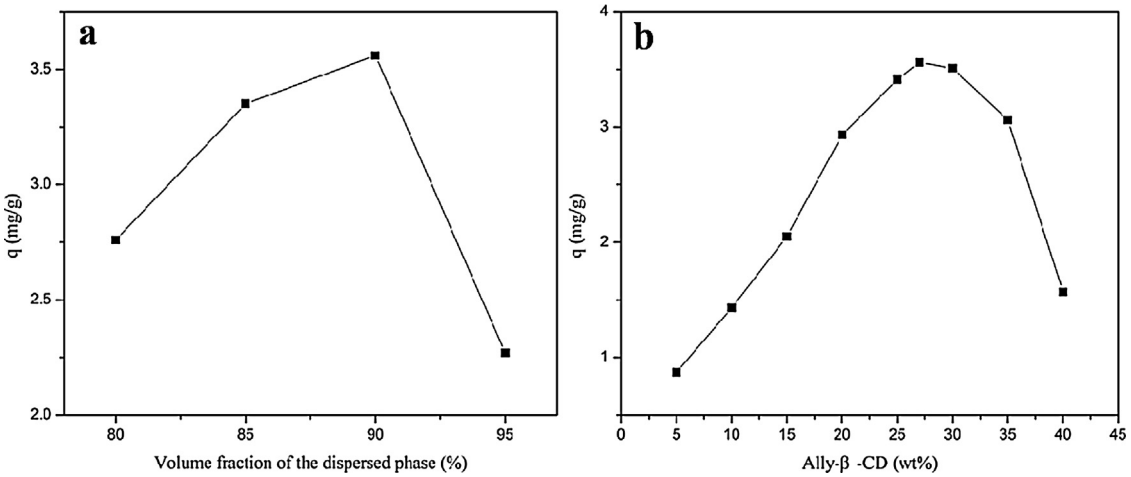

Fig. 5. Effect on the adsorption capacity for phenol of (a) the volume fraction of dispersed phase and (b) the allyl-β-CD content.

value. This gradual increase could be due to competition between H^+ interactions and phenol hydrogen bonding to the oxygen moieties in the β-CD (Dąbrowski, Podkościelny, Hubicki, & Barczak, 2005; Liu, Zheng, Wang, Jiang, & Li, 2010). As the pH increases, the competition from H^+ decreases. However, when pH was above 4.0, the adsorption capacity decreased with increasing pH value. This change could be attributed in part to the degree of ionization of phenols in aqueous solution. When the pH > pKa of the phenol, the phenol is predominantly in the ionized form that does not interact as well with the β-CD through hydrogen bonding. In addition, the negative phenolate ion has a greater solubility in water and thus partitions less into the host β-CD groups (Zhou et al., 2014). These effects combine to result in a low adsorption at high pH value.

3.6. Regeneration of porous monoliths.

For practical applications, the adsorbent should possess long-term stability and be able to undergo multiple adsorption/desorption cycles without loss of function (Mohamed, Wilson, & Headley, 2010). Such regenerability was tested here in a

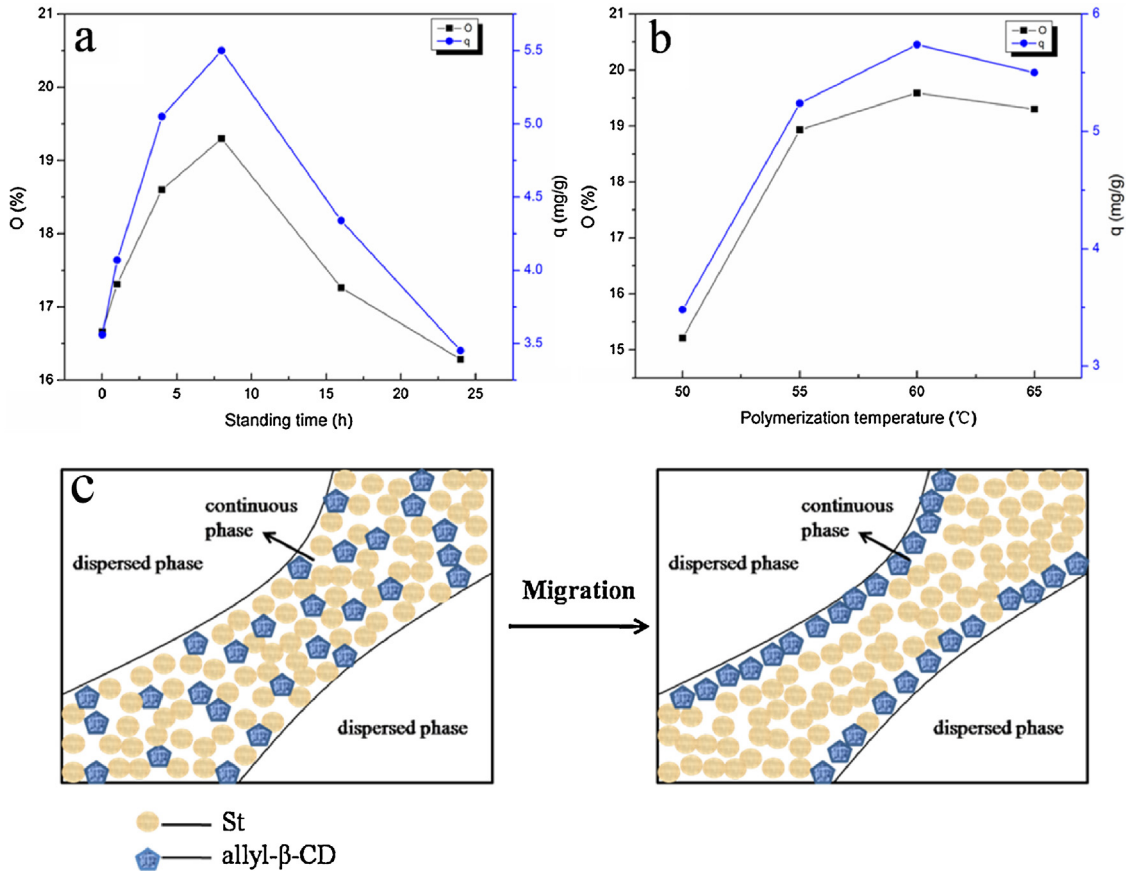

Fig. 6. (a) Effect of standing time and (b) polymerization temperature on surface oxygen content and adsorption capacity; (c) illustration of the migration of allyl-β-CD to the W/O interface of the polymerization emulsion.

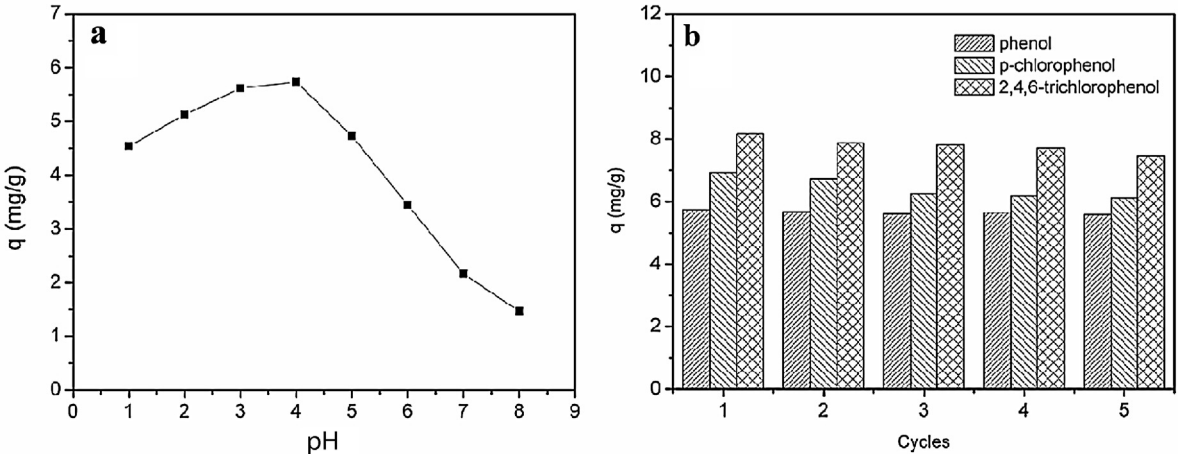

Fig. 7. (a) The adsorption behaviour of phenol as a function of solution pH and (b) the adsorption of phenol and two chlorophenol derivatives following repeated regeneration cycles.

chromatography column using ethanol as a desorbing agent. The test environment employed the same conditions of pH 4.0, 25 °C and 200 mg/L initial concentrations for phenol and two derivertives, p-chlorophenol and 2,4,6-trichlorophenol. The adsorption capacities for the first cycle were 5.74, 6.93, and 8.16 mg/g, respectively and it was found that this decreased only slightly after five cycles (Fig. 7b). Therefore, the β-CD functionalized porous monoliths are of potential value in industrial applications due to their ability to be effectively regenerated and their high phenol adsorption capacity.

4. Conclusions

The β-CD functionalized polystyrene porous monolith could be used as an efficient adsorbent for the removal of various phenols from wastewater. When it was prepared by concentrated emulsion copolymerization, it was found that the volume fraction of dispersed phase and the content of β-CD in the continuous phase significantly affects the stability of the emulsion, the specific surface area of the porous monolith, and consequently the adsorption capacity of phenol. This can be attributed to the migration of β-CD groups in the continuous phase during the polymerization process leading to a β-CD enriched W/O interface which enhances the adsorption capacity. The standing time after formation of the polymerization emulsion and the polymerization temperature both influence the migration of β-CD groups, and thus the adsorption capacity of the monolith. Optimum conditions were found when the standing time and the polymerization temperature were 8 h and 60 °C, respectively. This led to an adsorption capacity for phenol of 5.74 mg/g and excellent regeneration properties.

Acknowledgments

The work was supported by Beijing Natural Science Foundation (No. 2122046). And we thank Dr. Andrew Glidle at the University of Glasgow for proofreading the manuscript.

References

Badruddoza, A. Z. M., Shawon, Z. B. Z., Tay, W. J. D., Hidajat, K., & Uddin, M. S. (2013). Fe_3O_4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater. *Carbohydrate Polymers*, *91*(1), 322–332.

Bibby, A., & Mercier, L. (2003). Adsorption and separation of water-soluble aromatic molecules by cyclodextrin-functionalized mesoporous silica. *Green Chemistry*, *5*(1), 15–19.

Bosch, F., Font, G., & Mañes, J. (1987). Ultraviolet spectrophotometric determination of phenols in natural and waste waters with iodine monobromide. *Analyst*, *112*(9), 1335–1337.

Chai, K., & Ji, H. (2012). Dual functional adsorption of benzoic acid from wastewater by biological-based chitosan grafted β-cyclodextrin. *Chemical Engineering Journal*, *203*(0), 309–318.

Chen, Q. Y., Xiao, J. B., Chen, X. Q., Jiang, X. Y., Yu, H. Z., & Xu, M. (2006). The adsorption of phenol, m-cresol and m-catechol on a β-cyclodextrin derivative-grafted chitosan and the removal of phenols from industrial wastewater. *Adsorption Science & Technology*, *24*(7), 547–557.

Dąbrowski, A., Podkościelny, P., Hubicki, Z., & Barczak, M. (2005). Adsorption of phenolic compounds by activated carbon – A critical review. *Chemosphere*, *58*(8), 1049–1070.

Del Valle, E. M. (2004). Cyclodextrins and their uses: A review. *Process Biochemistry*, *39*(9), 1033–1046.

Eskandani, Z., Huin, C., & Guégan, P. (2011). Regioselective allylation of cyclomaltoheptaose (β-cyclodextrin) leading to per (2,6-di-O-hydroxypropyl-3-O-methyl)-β-cyclodextrin. *Carbohydrate Research*, *346*(15), 2414–2420.

Han, J., Du, Z., Zou, W., Li, H., & Zhang, C. (2014). Fabrication of interfacial functionalized porous polymer monolith and its adsorption properties of copper ions. *Journal of Hazardous Materials*, *276*, 225–231.

Hedges, A. R. (1998). Industrial applications of cyclodextrins. *Chemical Reviews*, *98*(5), 2035–2044.

Hergert, L., & Escandar, G. (2003). Spectrofluorimetric study of the β-cyclodextrin–ibuprofen complex and determination of ibuprofen in pharmaceutical preparations and serum. *Talanta*, *60*(2), 235–246.

Jiang, Y., Du, L., Lu, F., Li, Z., Yang, J., Bie, S., et al. (2006). Synthesis and properties of functionalized β-cyclodextrin copolymer and its metal complexes. *Polymer Bulletin*, *57*(4), 481–489.

Liu, Q.-S., Zheng, T., Wang, P., Jiang, J.-P., & Li, N. (2010). Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. *Chemical Engineering Journal*, *157*(2-3), 348–356.

Mohamed, M. H., Wilson, L. D., & Headley, J. V. (2010). Estimation of the surface accessible inclusion sites of β-cyclodextrin based copolymer materials. *Carbohydrate Polymers*, *80*(1), 186–196.

Prabaharan, M., & Gong, S. (2008). Novel thiolated carboxymethyl chitosan-g-β-cyclodextrin as mucoadhesive hydrophobic drug delivery carriers. *Carbohydrate Polymers*, *73*(1), 117–125.

Pulko, I., & Krajnc, P. (2012). High internal phase emulsion templating – A path to hierarchically porous functional polymers. *Macromolecular Rapid Communications*, *33*(20), 1731–1746.

Rekharsky, M. V., & Inoue, Y. (1998). Complexation thermodynamics of cyclodextrins. *Chemical Reviews*, *98*(5), 1875–1918.

Rolison, D. R. (2003). Catalytic nanoarchitectures – The importance of nothing and the unimportance of periodicity. *Science*, *299*(5613), 1698–1701.

Romo, A., Penas, F. J., Isasi, J. R., Garcia-Zubiri, I. X., & Gonzalez-Gaitano, G. (2008). Extraction of phenols from aqueous solutions by β-cyclodextrin polymers. Comparison of sorptive capacities with other sorbents. *Reactive and Functional Polymers*, *68*(1), 406–413.

Schneider, H.-J., Hacket, F., Rüdiger, V., & Ikeda, H. (1998). NMR studies of cyclodextrins and cyclodextrin complexes. *Chemical Reviews*, *98*(5), 1755–1786.

Schofield, W., Bain, C., & Badyal, J. (2012). Cyclodextrin-functionalized hierarchical porous architectures for high-throughput capture and release of organic pollutants from wastewater. *Chemistry of Materials*, *24*(9), 1645–1653.

Sun, Z. Y., Shen, M. X., Cao, G. P., Deng, J., Liu, Y., Liu, T., et al. (2010). Preparation of bimodal porous copolymer containing β-cyclodextrin and its inclusion adsorption behavior. *Journal of Applied Polymer Science*, *118*(4), 2176–2185.

Szejtli, J. (1998). Introduction and general overview of cyclodextrin chemistry. *Chemical Reviews*, *98*(5), 1743–1754.

Van de Manakker, F., Vermonden, T., van Nostrum, C. F., & Hennink, W. E. (2009). Cyclodextrin-based polymeric materials: Synthesis, properties, and pharmaceutical/biomedical applications. *Biomacromolecules*, *10*(12), 3157–3175.

Yamasaki, H., Makihata, Y., & Fukunaga, K. (2006). Efficient phenol removal of wastewater from phenolic resin plants using crosslinked cyclodextrin particles. *Journal of Chemical Technology and Biotechnology*, *81*(7), 1271–1276.

Yamasaki, H., Makihata, Y., & Fukunaga, K. (2008). Preparation of crosslinked β-cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater. *Journal of Chemical Technology and Biotechnology*, *83*(7), 991–997.

Yang, Y., Wei, Z., Wang, C., & Tong, Z. (2013). Lignin-based pickering HIPEs for macroporous foams and their enhanced adsorption of copper(II) ions. *Chemical Communications*, *49*(64), 7144–7146.

Yilmaz, E., Memon, S., & Yilmaz, M. (2010). Removal of direct azo dyes and aromatic amines from aqueous solutions using two β-cyclodextrin-based polymers. *Journal of Hazardous Materials*, *174*(1), 592–597.

Zhou, L.-C., Meng, X.-G., Fu, J.-W., Yang, Y.-C., Yang, P., & Mi, C. (2014). Highly efficient adsorption of chlorophenols onto chemically modified chitosan. *Applied Surface Science*, *292*(0), 735–741.

Zou, H., Huang, X., Ye, M., & Luo, Q. (2002). Monolithic stationary phases for liquid chromatography and capillary electrochromatography. *Journal of Chromatography A*, *954*(1), 5–32.