

A novel β -cyclodextrin polymer modified by sulfonate groups

Dong Zhao · Liang Zhao · Cheng-Shen Zhu ·
Jing Wang · Xiang-Hua Lv

Received: 23 January 2011 / Accepted: 19 July 2011 / Published online: 13 August 2011
© Springer Science+Business Media B.V. 2011

Abstract Based on the special properties and advantages of β -cyclodextrin (β -CD), β -CD polymers have been widely studied and used in recent years. A lot of researches have focused on the adsorption and separation properties of β -CD polymers. In this paper, β -CD polymer modified by sulfonate groups, which was named S- β -CDP, was prepared using epichlorohydrin as crosslinker and tiron (1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt) as modifier. β -CD polymer without modification, which was named β -CDP, was also prepared for comparison. Infrared spectra, elemental analysis and adsorption tests of S- β -CDP were carried out and compared with β -CDP. The content of sulfonate groups in S- β -CDP was obtained from elemental analysis. The dramatically increased adsorption capability toward methylene blue and basic magenta confirmed the existence and chemical activity of sulfonate groups in S- β -CDP. Due to the convenient preparation process and modified adsorption properties, S- β -CDP will find its applications in various fields such as water purification, drug loading, separation and analysis.

Keywords β -Cyclodextrin (β -CD) · β -Cyclodextrin polymer · Sulfonate groups · Tiron · Adsorption

Introduction

β -Cyclodextrin (β -CD) is a torus-shaped cyclic oligosaccharide made up of seven glucose units. The chemical structure of β -CD is shown in Fig. 1. The outside of β -CD is hydrophilic while the interior cavity of it is hydrophobic. Thus, β -CD can form inclusion complexes with guest molecules or ions, especially when the size of a guest well matches the cavity. β -CD is non-toxic to human body and easily degraded in the nature. Furthermore, β -CD has been largely produced and become inexpensive owing to the progressed production techniques. Because of these advantages, β -CD has been widely used in many fields including pharmaceuticals, foods, cosmetics, chemical products and technologies [1–7].

Based on the special properties and advantages of β -CD, β -CD polymers have also been widely studied in recent years. As has been reported, β -CD polymers can effectively adsorb organic molecules and heavy metals in water [8–20]. β -CD polymers modified by carboxyl/carboxylate groups ($-\text{COOH}/-\text{COO}^-$) have been found to be more efficient in adsorption toward some heavy metals, basic dyes and aromatic amines [21–30]. The improvements are ascribed to the chemical adsorption properties of carboxyl/carboxylate groups. Based on the similar mechanisms, sulfo/sulfonate groups ($-\text{SO}_3\text{H}/-\text{SO}_3^-$) were supposed by us to improve the adsorption properties of β -CD polymer as well.

In this paper, β -CD polymer modified by sulfonate groups, named S- β -CDP, was prepared using epichlorohydrin as crosslinker and tiron (1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt) as modifier. β -CD polymer without modification, named β -CDP, was also prepared for comparison. The preparation of S- β -CDP was designed as a successive one-pot process. Through copolymerization

D. Zhao · L. Zhao (✉) · J. Wang
Institute of Chemistry, Henan Academy of Sciences,
Zhengzhou 450002, China
e-mail: gszhaodong@163.com

C.-S. Zhu · X.-H. Lv
School of Materials Science and Engineering,
Zhengzhou University, Zhengzhou 450052, China

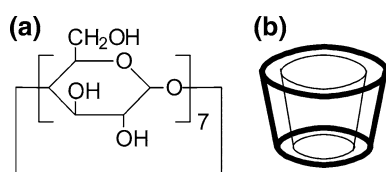


Fig. 1 Chemical structure (a) and shape (b) of β -cyclodextrin

reaction, the sulfonate groups of tiron were introduced into the structure of *S*- β -CDP. Tiron, which has two sulfonate groups and two hydroxyl groups on one benzene ring, is a normally used and inexpensive chemical reagent. The chemical structure of tiron is shown in Fig. 2. The hydroxyl groups of tiron can polymerize with epichlorohydrin similarly as the hydroxyl groups of β -CD.

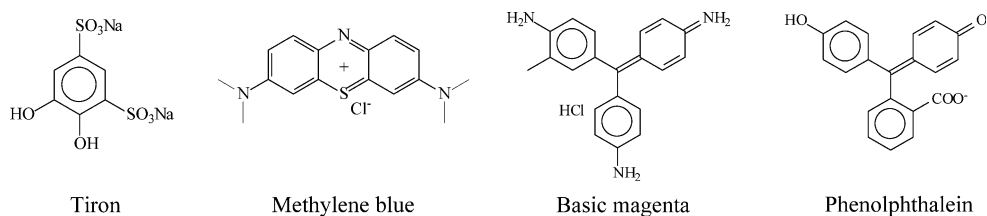
Infrared spectroscopy, elemental analysis and adsorption tests were employed to characterize the sulfonate groups in *S*- β -CDP. Methylene blue, basic magenta and phenolphthalein (as shown in Fig. 2) were selected to be adsorbed. Methylene blue and basic magenta are both basic dyes which can contaminate water and soil. The cationic groups (i.e. amino groups) of Methylene blue and basic magenta can be adsorbed by polymers with anionic groups (e.g. sulfo/sulfonate and carboxyl/carboxylate groups). Phenolphthalein is a well-known pH indicator whose molecular structure is alike to basic magenta. The major difference is that phenolphthalein has one carboxyl group while basic magenta has three amino groups.

Experimental

Materials

β -CD is a biochemical reagent (purity $\geq 99.0\%$) purchased from Tianjin Bodi Chemical Co., Ltd., China. Epichlorohydrin, tiron, sodium hydroxide, methylene blue, basic magenta and phenolphthalein are analytical pure reagents purchased from guaranteed manufacturers in China. Potassium bromide (KBr) used for Fourier-transform Infrared (FT-IR) is a spectrum pure reagent purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

Fig. 2 Chemical structures of the reagents used



Preparation of *S*- β -CDP

S- β -CDP was prepared through a successive one-pot process. Firstly, 1.5 g (4.77 mmol) of tiron and 1 g of sodium hydroxide were carefully dissolved in 5 mL of deionized water, then 2 mL (2.35 g, 25.4 mmol) of epichlorohydrin was added, and the mixture was stirred at 35–40 °C for 1 h to make solution A. Secondly, 10 g (8.81 mmol) of β -CD and 5 g of sodium hydroxide were carefully dissolved in 20 mL of deionized water to make solution B, then solution A and solution B were mixed together and stirred at 35–40 °C for 1.5 h to make solution C. Thirdly, 11 mL (12.9 g, 140 mmol) of epichlorohydrin was added into solution C, and the mixture was stirred at 35–40 °C for about 3 h until solid gel was formed. After aged for more than 10 h, the solid gel was broken into particles, soaked and washed thoroughly with hot water for several times to remove unreacted monomers, and dried at 50 °C with an electric thermostatic oven (DHG-9030A, Shanghai Jinghong Laboratory Instrument Co., Ltd, China).

For comparison, β -CDP (β -CD polymer without modification) was also prepared. 10 g (8.81 mmol) of β -CD was dissolved in 20 mL of 20% NaOH aqueous solution. 12 mL (14.1 g, 153 mmol) of epichlorohydrin was added into the solution and the mixture was stirred at 35–40 °C for about 3 h until solid gel was formed. After aged for more than 10 h, the solid gel was broken into particles, soaked and washed thoroughly with hot water for several times to remove unreacted monomers, and dried at 50 °C with the electric thermostatic oven.

FT-IR spectra

Small amount of sample was ground with KBr in an agate mortar and pressed into thin tablets under 16 MPa pressure using a manual hydraulic press (FW-4A, Tianjin Tuopu Instrument Co., Ltd., China). FT-IR spectra of the tablets were measured using an FT-IR spectrometer (Thermo Nicolet IR 200, Thermo Electron Corp., USA).

Elemental analysis

Small amount of sample was ground into powder in an agate mortar. 2 mg of the powder was precisely weighed

and used for analysis. The contents of C, H, N and S of the sample were determined by an elemental analyzer (Model 1106, Carlo-Erba, Italy).

Adsorption tests

Adsorption of methylene blue

0.1 g of particles (diameter smaller than 0.5 mm) of S- β -CDP or β -CDP was put into a conical flask containing 50 mL of methylene blue aqueous solution. The flask was shaken in a water bath shaker (SHA-C, Jintan Ronghua Instrument Manufacture Co., Ltd., China) at 30 °C for different time intervals. The absorbance ($\lambda_{max} = 665$ nm) of the solution at each time point was measured with a spectrophotometer (721 type, Shanghai Analytical Instruments Factory, China). Standard solutions were measured simultaneously to make a calibration curve. The concentration (C , mg L⁻¹) of methylene blue was calculated according to the absorbance value and the calibration curve. The adsorption quantity (q , mg g⁻¹) was calculated from C according to Eq. (1) as follows,

$$q_t = \frac{V(C_0 - C_t)}{W} \quad (1)$$

where q_t (mg g⁻¹) is the adsorption quantity per gram of adsorbent at time point t , $V(L)$ is the volume of solution, C_0 (mg L⁻¹) is the initial concentration, C_t (mg L⁻¹) is the concentration at time point t , and W (g) is the weight of adsorbent.

Adsorption of basic magenta

0.1 g of particles (diameter smaller than 0.5 mm) of S- β -CDP or β -CDP was put into a conical flask containing 50 mL of basic magenta aqueous solution. The flask was shaken in the water bath shaker at 30 °C for different time intervals. The absorbance ($\lambda_{max} = 543$ nm) of the solution at each time point was measured with the spectrophotometer. Standard solutions were measured simultaneously to make a calibration curve. The concentration (C , mg L⁻¹) and the adsorption quantity (q , mg g⁻¹) were calculated as described in “Adsorption of methylene blue”.

Adsorption of phenolphthalein

0.025 g of particles (diameter smaller than 0.5 mm) of S- β -CDP or β -CDP was put into a conical flask containing 50 mL of phenolphthalein aqueous solution (pH adjusted to 10.5 by Na₂CO₃ solution). The flask was shaken in the water bath shaker at 30 °C for different time intervals. The absorbance ($\lambda_{max} = 552$ nm) of the solution at each time point was measured with the spectrophotometer. Standard

solutions were measured at the same time to make a calibration curve. The concentration (C , mg L⁻¹) and the adsorption quantity (q , mg g⁻¹) were calculated as described in “Adsorption of methylene blue”.

Results and discussion

Preparation of S- β -CDP and β -CDP

The reaction mechanism of the preparation of S- β -CDP was illustrated in Fig. 3. Our previous experiments showed that if the crosslinking reaction was performed in just one step, the reaction mixture was not crosslinked together but remained fluid. The crosslinking reaction was inhibited by the addition of tiron, because tiron was a small molecule which has only two -OH groups. Thus, the preparation was designed as a successive three-step process: step 1, tiron reacted with excessive epichlorohydrin to produce an intermediate with both sulfonate groups and epoxy groups; step 2, β -CD was added and the intermediate was grafted onto β -CD; step 3, enough epichlorohydrin was added and the modified and unmodified β -CD molecules were cross-linked into polymer. The reaction mechanisms is shown in Fig. 3.

14.2 g of S- β -CDP (β -CD polymer modified by sulfonate groups) was obtained when 10 g of β -CD and 1.5 g of tiron were used for preparation. S- β -CDP was a water-insoluble white solid, easy to be ground into small particles. When swelled in water at room temperature, S- β -CDP got a weight increase of 77%, indicating its good hydrophilicity.

14.6 g of β -CDP (β -CD polymer without modification) was obtained when 10 g of β -CD was used for preparation. β -CDP was also a water-insoluble and easily ground white solid. When swelled in water, β -CDP got a weight increase of 46% which was lower than S- β -CDP. The modification by tiron improved the hydrophilicity of S- β -CDP, probably

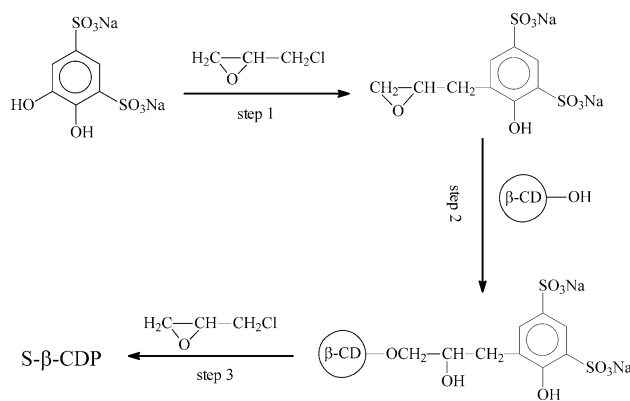


Fig. 3 Reaction mechanism of the preparation of S- β -CDP

because the introduced sulfonate groups are highly hydrophilic groups which are completely ionized in water, or/and because the crosslinking degree of *S*- β -CDP was decreased by the modifier which is a much smaller molecule than β -CD.

With the addition of tiron, the yield of *S*- β -CDP was not considerably decreased, indicating that the preparation process of *S*- β -CDP was practicable.

FT-IR spectra of β -CD, *S*- β -CDP and β -CDP

The FT-IR spectra of β -CD, *S*- β -CDP and β -CDP are shown in Fig. 4. The O–H stretching vibration at $3,400\text{ cm}^{-1}$, the C–H stretching vibration at $2,925\text{ cm}^{-1}$, the C–OH stretching vibration at $1,030\text{ cm}^{-1}$ and other adsorption peaks in the spectrum of β -CD also appeared nearly at the same wavenumbers in the spectra of *S*- β -CDP and β -CDP, indicating that *S*- β -CDP and β -CDP are made up chiefly by β -CD units. Compared with β -CDP, *S*- β -CDP exhibited a broader O–H stretching vibration (at $3,437\text{ cm}^{-1}$), a stronger O–H deformation vibration (at $1,639\text{ cm}^{-1}$) and a weaker C–O stretching vibration (at $1,043\text{ cm}^{-1}$), probably because the O–H and C–O bonds in the polymer were influenced by the introduced sulfonate groups. The typical adsorption peaks of sulfonate groups (S=O stretching vibrations at $1,250$ – $1,150\text{ cm}^{-1}$ and $1,100$ – $1,000\text{ cm}^{-1}$) were absent (perhaps overlapped by other peaks) in the spectrum of *S*- β -CDP. But the strengthened O–H deformation vibration at $1,401\text{ cm}^{-1}$

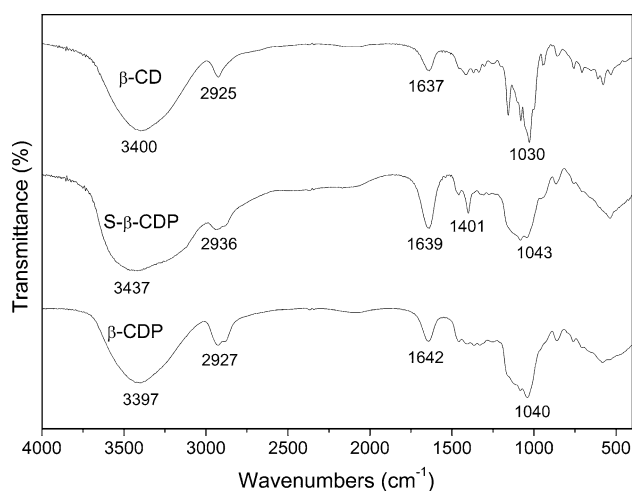


Fig. 4 FT-IR spectra of β -CD, *S*- β -CDP and β -CDP

indicated the existence of hydroxyl groups different from β -CD or β -CDP. Tiron introduced into the polymer might have provided these different hydroxyl groups or have influenced the O–H deformation of β -CD polymer. Due to the complexity of IR spectra of β -CD polymers, other test methods were required to further characterize the sulfonate groups in *S*- β -CDP.

Elemental analysis of *S*- β -CDP and β -CDP

The contents of C, H, N and S (carbon, hydrogen, nitrogen and sulfur) of *S*- β -CDP and β -CDP were obtained from elemental analysis, as shown in Table 1. According to the content of S, *S*- β -CDP has 0.174 mmol of sulfonate groups per gram of polymer. The C/H ratios of *S*- β -CDP (6.63) and β -CDP (6.59) are close to each other, indicating that the chief constituents of them are similar to each other.

Adsorption tests of *S*- β -CDP and β -CDP

To further testify the existence and chemical activity of the sulfonate groups of *S*- β -CDP, adsorption tests toward methylene blue, basic magenta and phenolphthalein were carried out respectively with *S*- β -CDP as adsorbent. For comparison, β -CDP was also tested under the same conditions. The adsorption results are shown in Figs. 5, 6 and 7. In each figure the left part is the concentration (*C*)–time (*t*) curve and the right part is the adsorption quantity (*q*)–time (*t*) curve.

As shown in Fig. 5, the adsorption of methylene blue by *S*- β -CDP was remarkably higher than β -CDP. In 360 min, the concentration of methylene blue was reduced from 9.15 mg L^{-1} to 0.67 mg L^{-1} by *S*- β -CDP and the adsorption quantity of *S*- β -CDP reached 4.24 mg g^{-1} ($0.0133\text{ mmol g}^{-1}$). β -CDP adsorbed methylene blue very slightly under the same condition. The adsorption quantity of β -CDP after 360 min was only 0.32 mg g^{-1} ($0.0010\text{ mmol g}^{-1}$). It is inferred that the amino groups of methylene blue were effectively adsorbed by the sulfonate groups of *S*- β -CDP.

As shown in Fig. 6, the adsorption of basic magenta by *S*- β -CDP was also much higher than β -CDP. In 210 min, the concentration of basic magenta was reduced from 4.83 mg L^{-1} to 0.27 mg L^{-1} by *S*- β -CDP and the adsorption quantity of *S*- β -CDP reached 2.28 mg g^{-1} ($0.0067\text{ mmol g}^{-1}$). The adsorption quantity of β -CDP after 210 min

Table 1 Elemental analysis of *S*- β -CDP and β -CDP

Sample	C (wt. %)	H (wt. %)	N (wt. %)	S (wt. %)	S (mmol/g)
<i>S</i> - β -CDP	44.77	6.750	0.000	0.556	0.174
β -CDP	46.18	7.007	0.000	0.000	0.000

Fig. 5 Adsorption of methylene blue by S- β -CDP and β -CDP ($C_0 = 9.15 \text{ mg L}^{-1}$, $V = 50 \text{ mL}$, $T = 30 \text{ }^\circ\text{C}$, $W = 0.1 \text{ g}$)

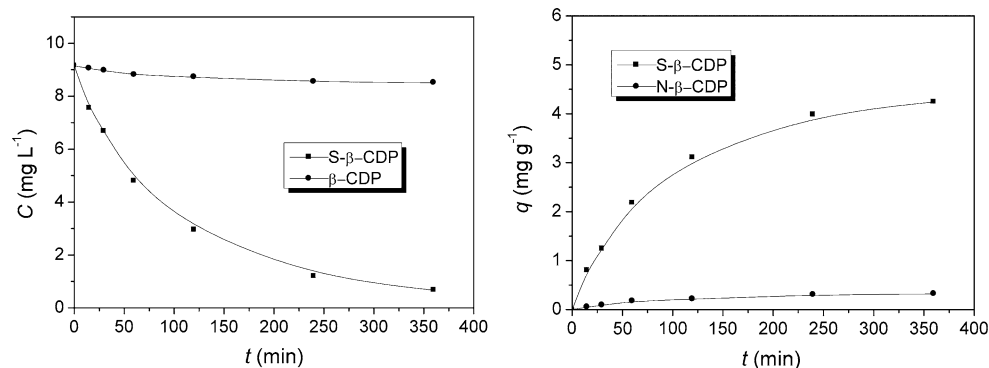


Fig. 6 Adsorption of basic magenta by S- β -CDP and β -CDP ($C_0 = 4.83 \text{ mg L}^{-1}$, $V = 50 \text{ mL}$, $T = 30 \text{ }^\circ\text{C}$, $W = 0.1 \text{ g}$)

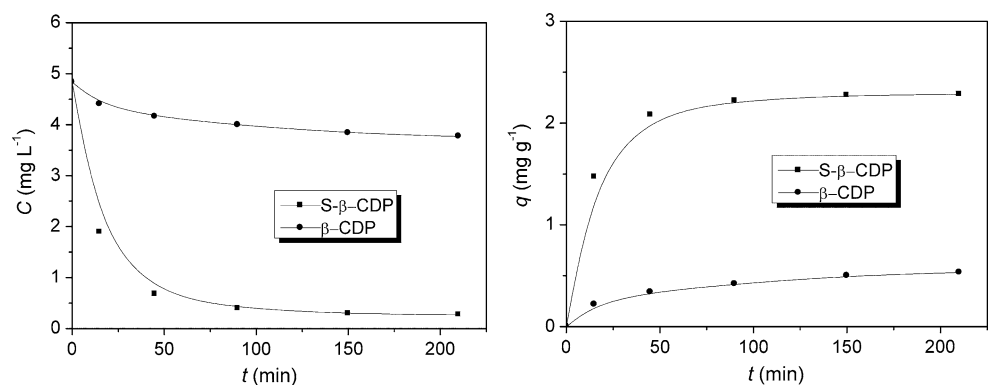
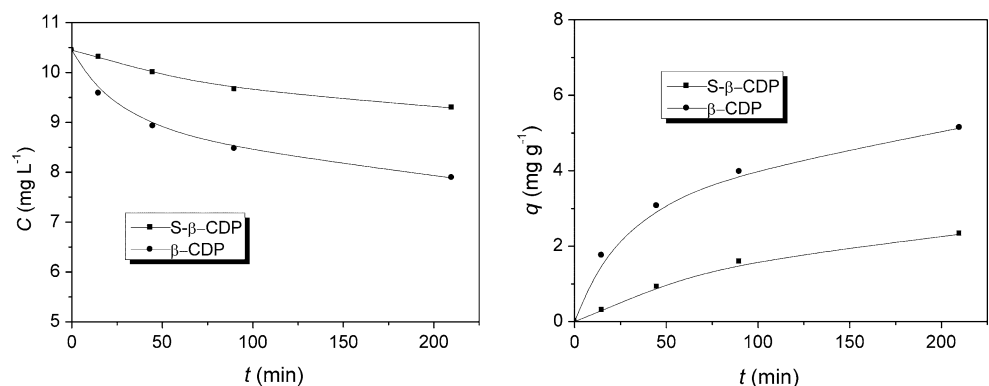


Fig. 7 Adsorption of phenolphthalein by S- β -CDP and β -CDP ($C_0 = 10.4 \text{ mg L}^{-1}$, $V = 50 \text{ mL}$, $T = 30 \text{ }^\circ\text{C}$, $W = 0.025 \text{ g}$)



under the same condition was 0.53 mg g^{-1} ($0.0016 \text{ mmol g}^{-1}$). It is inferred that the amino groups of basic magenta were effectively adsorbed by the sulfonate groups of S- β -CDP. Because basic magenta matches the cavity of β -CD better than methylene blue does, β -CDP also showed a considerable adsorption toward basic magenta.

As shown in Fig. 7, the adsorption of phenolphthalein by S- β -CDP was lower than β -CDP. After 210 min, the adsorption quantity values of S- β -CDP and β -CDP were 2.32 mg g^{-1} ($0.0073 \text{ mmol g}^{-1}$) and 5.13 mg g^{-1} ($0.0162 \text{ mmol g}^{-1}$) respectively. As has been known, the molecular size of phenolphthalein matches β -CD well, thereby phenolphthalein can be adsorbed by the β -CD cavities of S- β -CDP or β -CDP. S- β -CDP exhibited a lower adsorption, perhaps because the carboxylate groups of phenolphthalein and the

sulfonate groups of S- β -CDP are both anionic groups and they repelled each other during adsorption.

The adsorption tests discussed above confirmed the existence and chemical activity of sulfonate groups in S- β -CDP. The results also disclosed that sulfonate groups could dramatically influence and improve the adsorption performances of β -CD polymer.

Conclusions

S- β -CDP, a novel β -CD polymer modified by sulfonate groups, was prepared using epichlorohydrin as crosslinker and tiron as modifier. β -CDP (β -CD polymer without modification) was also prepared for comparison. Compared

with β -CDP, the yield of *S*- β -CDP was not considerably reduced by the addition of tiron. FT-IR spectra showed that the basic structure of *S*- β -CDP is alike to β -CDP and some differences exist due to modification. Elemental analysis showed that *S*- β -CDP contained 0.174 mmol g⁻¹ of sulfonate groups. Adsorption tests toward methylene blue, basic magenta and phenolphthalein confirmed the existence and chemical activity of sulfonate groups in *S*- β -CDP. Due to the convenient preparation process and modified adsorption properties, *S*- β -CDP will find its applications in various fields such as water purification, drug loading, separation and analysis.

Acknowledgments We gratefully acknowledge the support of the Important Public welfare Research Project of Henan Province, China. We sincerely thank Mr. Weiqing Huang, Mr. Zhenbang Tian and Mr. Zuohua Huang for their kind helps.

References

- Szejtli, J.: Cyclodextrin Technology, 1st edn. Kluwer Academic Publishers, Dordrecht (1988)
- Szejtli, J.: Utilization of cyclodextrins in industrial products and processes. *J. Mater. Chem.* **7**(4), 575–587 (1997)
- Szejtli, J.: Introduction and general overview of cyclodextrin chemistry. *Chem. Rev.* **98**(5), 1743–1754 (1998)
- Shieh, W.J., Hedges, A.R.: Properties and applications of cyclodextrins. *J. Macromol. Sci. A* **33**(5), 673–683 (1996)
- Hedges, A.R.: Industrial applications of cyclodextrins. *Chem. Rev.* **98**(5), 2035–2044 (1998)
- Martin Dell Valle, E.M.: Cyclodextrins and their uses: a review. *Process Biochem.* **39**(9), 1033–1046 (2004)
- Manakker, F.V.D., Vermonden, T., Nostrum, C.F.V., et al.: Cyclodextrin-based polymeric materials: synthesis, properties, and pharmaceutical biomedical applications. *Biomacromolecules* **10**(12), 3157–3175 (2009)
- Harada, A., Furue, M., Nozakura, S.-I.: Inclusion of aromatic compounds by a β -cyclodextrin-epichlorohydrin polymer. *Polym. J.* **13**(8), 777–781 (1981)
- Shao, Y., Martel, B., Morcellet, M., et al.: Sorption of textile dyes on β -cyclodextrin-epichlorohydrin gels. *J. Incl. Phenom. Macrocycl. Chem.* **25**(1–3), 209–212 (1996)
- Werner, T.C., Iannacone, J.L., Amoo, M.N.: The binding of pyrene and other probes to CD polymers. *J. Incl. Phenom. Macrocycl. Chem.* **25**(1), 77–80 (1996)
- Crini, G., Bertini, S., Torri, G., et al.: Sorption of aromatic compounds in water using insoluble cyclodextrin polymers. *J. Appl. Polym. Sci.* **68**(12), 1973–1978 (1998)
- Crini, G., Morcellet, M.: Synthesis and applications of adsorbents containing cyclodextrins. *J. Sep. Sci.* **25**(13), 789–813 (2002)
- Kitaoka, M., Hayashi, K.: Adsorption of bisphenol A by cross-linked β -cyclodextrin polymer. *J. Incl. Phenom. Macrocycl. Chem.* **44**(1), 429–431 (2002)
- Crini, G.: Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **30**(1), 38–70 (2005)
- Crini, G.: Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol.* **97**(9), 1061–1085 (2006)
- Gu, T., Tsai, G., Tsao, G.T.: Synthesis of rigid cyclodextrin-containing polymeric resins for adsorption. *J. Incl. Phenom. Macrocycl. Chem.* **56**(3), 375–379 (2006)
- Yamasaki, H., Makihata, Y., Fukunaga, K.: Preparation of crosslinked β -cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater. *J. Chem. Technol. Biotechnol.* **83**, 991–997 (2008)
- Romo, A., Pe, F.J., Isasi, J.R., et al.: Extraction of phenols from aqueous solutions by β -cyclodextrin polymers. Comparison of sorptive capacities with other sorbents. *React. Funct. Polym.* **68**(1), 406–413 (2008)
- Sun, Z.Y., Cao, G.P., Lv, H., et al.: Equilibrium of benzidine inclusion adsorption on cyclodextrin copolymer. *J. Appl. Polym. Sci.* **114**, 3882–3888 (2009)
- Li, N., Mei, Z., Ding, S.G.: 2,4-Dichlorophenol sorption on cyclodextrin polymers. *J. Incl. Phenom. Macrocycl. Chem.* **68**(1–2), 123–129 (2010)
- Martel, B., Morcellet, M., Ruffin, D., et al.: Finishing of polyester fabrics with cyclodextrins and polycarboxylic acids as cross-linking agents. *J. Incl. Phenom. Macrocycl. Chem.* **44**(1), 443–446 (2002)
- Crini, G., Peindy, H.N.: Adsorption of C.I. Basic Blue 9 on cyclodextrin-based material containing carboxylic groups, dyes pigments **70**(3), 204–211 (2006)
- Ducoroy, L., Martel, B., Bacquet, B., et al.: Ion exchange textiles from the finishing of PET fabrics with cyclodextrins and citric acid for the sorption of metallic cations in water. *J. Incl. Phenom. Macrocycl. Chem.* **57**(1), 271–277 (2007)
- El Ghoul, Y.: Martel B., Morcellet M.: Mechanical and physico-chemical characterization of cyclodextrin finished polyamide fibers. *J. Incl. Phenom. Macrocycl. Chem.* **57**, 47–52 (2007)
- Girek, T., Shin, D.H., Lim, S.T.: Polymerization of β -cyclodextrin with maleic anhydride and structural characterization of the polymers. *Carbohydr. Polym.* **42**(1), 59–63 (2000)
- Girek, T., Kozłowski, C.A., Koziol, J.J., et al.: Polymerisation of β -cyclodextrin with succinic anhydride. Synthesis, characterisation, and ion flotation of transition metals. *Carbohydr. Polym.* **59**(2), 211–215 (2005)
- Berto, S., Bruzzoniti, M.C., Cavalli, R., et al.: Synthesis of new ionic β -cyclodextrin polymers and characterization of their heavy metals retention. *J. Incl. Phenom. Macrocycl. Chem.* **57**, 631–636 (2007)
- Berto, S., Bruzzoniti, M.C., Cavalli, R., et al.: Highly crosslinked ionic β -cyclodextrin polymers and their interaction with heavy metals. *J. Incl. Phenom. Macrocycl. Chem.* **57**(1), 637–643 (2007)
- Zhao, D., Zhao, L., Zhu, C.S., et al.: Water-insoluble β -cyclodextrin polymer crosslinked by citric acid: Synthesis and adsorption properties toward phenol and methylene blue. *J. Incl. Phenom. Macrocycl. Chem.* **63**(3–4), 195–201 (2009)
- Zhao, D., Zhao, L., Zhu, C.S., et al.: Comparative study of polymer containing β -cyclodextrin and-COOH for adsorption toward aniline, 1-naphthylamine and methylene blue. *J. Hazard. Mater.* **171**(1–3), 241–246 (2009)