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Synthesis and properties of water-insoluble β-cyclodextrin polymer crosslinked by citric acid with PEG-400 as modifier

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ABSTRACT

Water-insoluble β-cyclodextrin polymer (β-CDP) crosslinked by citric acid was synthesized with Polyethylene glycol 400 (PEG-400) as modifier through an environment friendly procedure. The yield of β-CDP was related to the amounts of citric acid, PEG-400 and catalyst in the formulation. β-CD content and total acidic groups of the produced β-CDP were also found to be related to the formulation. FT-IR spectra disclosed that the hydroxyl groups of β-CD had crosslinked with the carboxyl groups of citric acid, and at the same time the structure characteristics of β-CD were well maintained in the polymer. Preliminary study on adsorption toward aniline disclosed that β-CDP which had a larger amount of total acidic groups generally had a larger adsorption capacity towards aniline.

1. Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The individual glucose units are held in a C-1 chair conformation and they are joined together by α-1,4 glycosidic linkages to form a cyclic structure. The interior cavity of CDs is relatively hydrophobic and the most characteristic feature of CDs is the ability to form inclusion complexes through host–guest interactions. The practically important, industrially produced CDs are α-, β- and γ-CDs, which are made up of six, seven and eight α-1,4-linked D-glucopyranose units, respectively. β-CD is the most largely produced cyclodextrin and has been widely used in many fields including pharmaceuticals, foods, cosmetics, chemical products and technologies (Fromming & Szejtli, 1994; Hedges, 1998; Kozlowski & Sliwa, 2008; Li & Purdy, 1992; Martin Dell Valle, 2004; Szejtli, 1988; Szejtli, 1997; Szejtli, 1998; Szejtli, 2003; Uekama, Hirayama, & Irie, 1998).

Water-insoluble β-cyclodextrin polymer (β-CDP) is a new type of adsorbent useful for removal of organic pollutants and heavy metals in water (Aoki, Nishikawa, & Hattori, 2003; Crini, 2005; Crini & Morcellet, 2002; Gaffar, El-Rafie, & El-Tahlawy, 2004; Gazpio et al., 2008; Prabaharan & Mano, 2006; Šimkovic, 2008; Vélaz, Isasi, Sánchez, Uzqueda, & Ponchel, 2007). The general method for synthesis of water-insoluble β-CDP is by crosslinking the hydroxyl groups of β-CDs with bi- or multi-functional molecules to form a stable crosslinked network. The bi- or multi-functional molecules used are normally called crosslinking agents. Effective crosslinking agents that have been reported include: epichlorohydrin (Crini et al., 1998, 1998a; Gu, Tsai, & Tsao, 2006; Harada, Furue, & Nozakura, 1981; Kitaoka & Hayashi, 2002; Shao, Martel, Morcellet, Weltrowski, & Crini, 1996; Werner, Iannacone, & Amoo, 1996), diisocyanates (Cadars, Foray, Gadelle, Gerbaud, & Bardet, 2005; Gerbaud, Hediger, Gadelle, & Bardet, 2008; Sreenivasan, 1996; Zha, Li, & Chang, 2008), polycarboxylic acids (Ducoroy, Martel, Bacquet, & Morcellet, 2007; El Ghoul et al., 2007; Fratoni & Baglioni, 2002; Martel, Morcellet, Ruffin, Ducoroy, & Weltrowski, 2002) and anhydrides (Berto et al., 2007, 2007a; Girek, Kozlowski, Koziol, Walkowiak, & Korus, 2005; Girek, Shin, & Lim, 2000). Epichlorohydrin is widely used in chemistry and industry, and is the most popularly used crosslinking reagent for β-CDP synthesis (Crini, 2005; Crini & Morcellet, 2002). But epichlorohydrin is a toxic and hazardous substance and is potentially harmful to human health and the environment (Crini, 2005). At the same time, a large portion of epichlorohydrin might be wasted in the reaction, because the reaction between β-CD and epichlorohydrin required a high concentration of sodium hydroxide which will accelerate the hydrolyzation of epichlorohydrin. Diisocyanates, such as toluene diisocyanate and hexamethylene diisocyanate, are also hazardous to human and environment, and organic solvents are required in the reaction between β-CD and diisocyanates. Comparatively, citric acid has a low toxicity and is more friendly to the environment (Wikipedia, 2009). The condensation between β-CD and citric acid can be performed at a temperature not higher than 200 °C and without any organic solvent or harmful additives, although the reactivity of citric acid is lower than epichlorohydrin or diisocyanates.

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Martel et al. has reported the synthesis and applications of β-CDP immobilized on natural or synthetic fabrics using polycarboxylic acid as the crosslinking agent and sodium dihydrogen hypophosphite as catalyst (Ducoroy et al., 2007; El Ghoul et al., 2007; Martel et al., 2002). The β-CDP immobilized on the fabrics has the ability to adsorb heavy metal ions (Pb^{2+}, Cd^{2+} and Ni^{2+}) from water because the carboxyl groups contained in β-CDP can serve as ion-exchange sites. β-CDP immobilized on the fabrics can also increase the period of release of perfumes and improve the resistance of the odor to washings with water.

In this paper, water-insoluble β-CDP was synthesized using citric acid monohydrate (CAM) as crosslinking agent, sodium dihydrogen phosphate (MSP) as catalyst and PEG-400 as modifier. The effects of CAM, MSP and PEG-400 on the yield (*Y*) and properties of β-CDP were examined by series of experiments. The structure of β-CDP was characterized by Fourier-transform infrared spectroscopy (FT-IR). The β-CD content (*TC*) of β-CDP, total acidic groups (*TA*) of β-CDP and adsorption capacity (*q*) toward aniline by β-CDP were examined respectively.

2. Experimental

2.1. Materials

β-Cyclodextrin is a biochemical reagent (purity ⩾99.0%) purchased from Tianjin Bodi Chemical Co., Ltd., China. Citric acid monohydrate (CAM), sodium dihydrogen phosphate (MSP), and aniline, are analytical pure reagents purchased from accredited manufacturers in China. Polyethylene glycol 400 (PEG-400) of molecular weight 370–460 was purchased from the Shanghai Chemical Reagents Company. Potassium bromide (KBr) used for FT-IR is a spectrum pure reagent purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

2.2. Synthesis of β-CDP

β-CD, PEG-400, citric acid monohydrate (CAM), sodium dihydrogen phosphate (MSP) and some deionized water were mixed in a round bottom flask and stirred in a boiling water bath. The mixture was transferred into a culture dish and heated in an electric thermostatic oven (DHG-9030A, Shanghai Jinghong Laboratory Instrument Co., Ltd., China) at 140 °C for 4 h.

Because the culture dish was wide open, the water was quickly driven away by heating. Then polymerization started, and the water generated during the reaction was instantly driven away, thus the equilibrium was pushed forward successively.

After naturally cooling, the crude product was weighed (recorded as W_c) and ground finely. The granules were purified by soaking and washing with deionized water several times, then suction filtered and dried at 50 °C to constant weight (recorded as W_p). W_p is the weight of the purified β-CDP, i.e. the weight of water-insoluble polymer in the product. The yield (*Y*) of the purified β-CDP was calculated as follows,

$$Y = \frac{W_c - W_p}{W_c} \times 100\% \tag{1}$$

2.3. FT-IR spectra of β-CDP

Small amount of β-CDP was mixed and ground thoroughly with KBr powder 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). Fourier-transform Infrared (FT-IR) spectra were measured using the tablets by a FT-IR spectrometer (Thermo Nicolet IR 200, Thermo Electron Corp., USA).

2.4. β-CD content of β-CDP

β-CD content of β-CDP was determined by phenolphthalein colorimetric method (Mäkelä et al., 1987; Basappa, Rao, Rao, & Divakar, 1998).

In order to calculate the β-CD concentration for each experiment, a calibration curve was first prepared. Different volume of β-CD standard solution was mixed with 2 mL of phenolphthalein standard solution (3.732×10^{-4} M) and 2 ml of Na_2CO_3 solution (0.028 M), and the mixed solution was diluted to 25 mL. Absorbance of the diluted solution was measured at 553 nm using a spectrophotometer (721 type, Shanghai Analytical Instruments Factory, China). The concentration values were plotted against the absorbance values to obtain a calibration curve which was fitted mathematically.

In each experiment, 0.1 g of finely powdered β-CDP was dissolved completely in 20 mL of 0.1 M NaOH solution. The resultant solution was neutralized to pH 7 by 0.1 M HCl solution and diluted to 100 mL (marked as S1). 5 mL of S1 was mixed with 2 mL of phenolphthalein standard solution (3.732×10^{-4} M) and 2 ml of Na_2CO_3 solution (0.028 M) and diluted to 25 mL (marked as S2). The absorbance (*A*) of S2 was measured at 553 nm using the spectrophotometer, and the corresponding β-CD concentration (*C*) was calculated from *A* according to the calibration equation. β-CD content (*TC*) of β-CDP was calculated as follows,

$$TC = \frac{C \times 5 \times V}{W} \times 100\% \tag{2}$$

Where *C* is the β-CD concentration of S2 ($g\,L^{-1}$); *V* is the volume of S1(L); and *W* is the weight of β-CDP (g).

2.5. Total acidic groups of β-CDP

The amount of total acidic groups (*TA*) of β-CDP, including carboxyl groups and ester groups, was determined by titration. 0.1 g of finely powdered β-CDP was put into a conical flask containing 20 mL of 0.1 M NaOH solution and stirred for 15 h at 30 °C. Thus, β-CDP was completely hydrolyzed and dissolved. The resulted solution was titrated with 0.1 M HCl solution until pH 7, pH measured using a digital pH meter (PHS-3E, Shanghai Precision & Scientific Instrument Co., Ltd.). *TA* of β-CDP was calculated as follows:

$$TA = \frac{C \times (V_0 - V_1)}{W} \tag{3}$$

where *C* is the concentration of HCl solution ($mmol\,L^{-1}$); V_0 is the volume of HCl solution consumed by blank solution (L); V_1 is the volume of HCl solution consumed by sample solution (L); and *W* is the weight of β-CDP (g).

2.6. Adsorption toward aniline by β-CDP

β-CD (0.1 g) was put into a conical flask containing 25 mL of aniline aqueous solution. The flask was well covered and shaken in a water bath shaker (SHA-C, Jintan Ronghua Instrument Manufacture Co., Ltd., China) at 30 °C for different time intervals. The *TN* (total nitrogen) value of the solution at different time point was determined by a multi-N/C 2100 *TOC/TN* analyzer (Analytik Jena AG, Germany). Since every aniline molecule contains one nitrogen atom, the concentration of aniline (*C*) was calculated from *TN*: $C = 6.65 \times TN$. The adsorption capacity (*q*) of β-CDP toward aniline was calculated as follows:

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{4}$$

where q_t ($mg\,g^{-1}$) is the adsorption capacity at contact time *t*, *V* is the volume of aniline solution (L), C_0 is the initial concentration of aniline (mg L^{-1}), C_t is the concentration of aniline at contact time t (mg L^{-1}), and W is the weight of β-CDP (g).

3. Results and discussion

Series of β-CDPs based on different formulations (as shown in Table 1) were synthesized through the same procedure and under the same conditions, as described in the experimental section. In formulations A1–5, only PEG-400 was of different amount. In B1–5, only MSP was of different amount. And in C1–5, only CAM was of different amount. Thus, the effects of PEG-400, MSP and CAM can be separately examined. D1, which was a β-CDP crosslinked by epichlorohydrin prepared according to the method of Harada et al. (1981), was also examined and compared with β-CDP crosslinked by citric acid.

3.1. Effects of formulation on yield (*Y*) of *β*-CDP

After polymerization and treatments as described in the experimental section, the yield (*Y*) of each product was calculated according to Eq. (1). Clear relationships were found between *Y* and the formulation. Fig. 1 showed that *Y* increased remarkably at first with the increase of CAM in the formulation, but increased not obviously when CAM was over 2 g. It was found that when CAM was over 3 g, the product would become very stiff and difficult to break. Thus, 2–3 g of CAM was preferred in formulations C1–5. Fig. 2 showed that *Y* reached a maximum value when PEG-400 was 1 g, then decreased remarkably with the increase of PEG-400. This indicated that suitable amount of PEG-400 was beneficial to the polymerization, while excessive PEG-400 was destructive. Fig. 3 showed that the presence of MSP improved *Y* remarkably, but *Y* didn't increase anymore when MSP was over 0.1 g. This indicated that suitable amount of catalyst was significant to the polymerization, while excessive catalyst was unnecessary.

3.2. *β*-CD content (*TC*) and total acidic groups (*TA*) of *β*-CDP

The β-CD content (*TC*) and total acidic groups (*TA*) of β-CDP were also found to relate to the formulation. As shown in Fig. 4 (C3, C4 and C5), when CAM in the formulation increased, *TA* increased remarkably, while *TC* decreased remarkably. As shown in Fig. 5 (A1, A2 and A3), when PEG-400 was 1 g (A2), *TC* reached a largest value, while *TA* reached a lowest value. These results indicated that not only the yield, but also the components of the produced β-CDPs, were strongly affected by the formulation.

Table 1
Formulations for the synthesis of β-CDPs.

Sample	β-CD (g)	PEG-400 (g)	MSP (g)	CAM (g)
A1	10	0	0.25	2
A2	10	1	0.25	2
A3	10	2	0.25	2
A4	10	3	0.25	2
A5	10	4	0.25	2
B1	10	1	0	2
B2	10	1	0.125	2
B3	10	1	0.25	2
B4	10	1	0.4	2
B5	10	1	0.5	2
C1	10	1	0.25	0.4
C2	10	1	0.25	1
C3	10	1	0.25	2
C4	10	1	0.25	3
C5	10	1	0.25	4
D1	Crosslinked by epichlorohydrin			

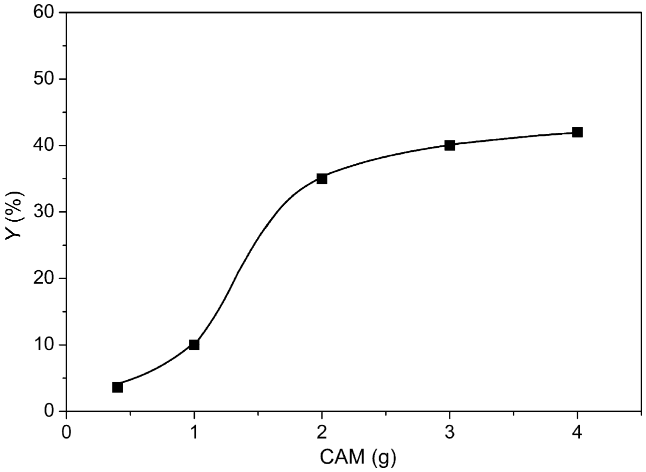

Fig. 1. Effect of CAM on the yield of β-CDP (C1–5 in Table 1).

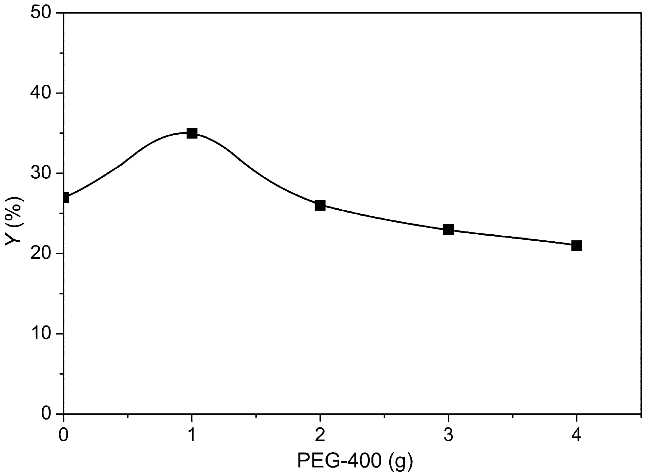

Fig. 2. Effect of PEG-400 on the yield of β-CDP (A1–5 in Table 1).

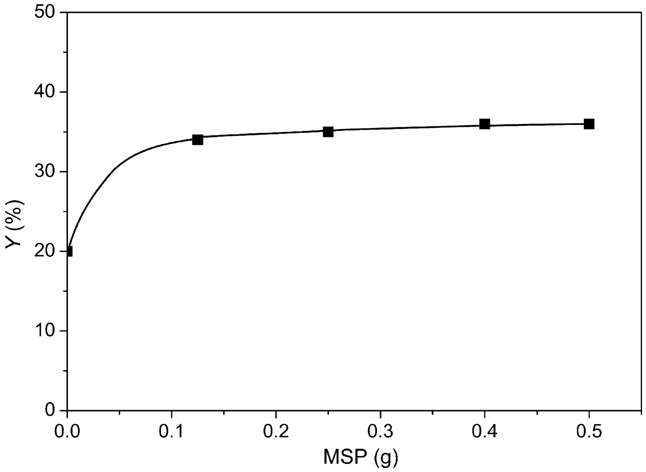

Fig. 3. Effect of MSP on the yield of β-CDP (B1–5 in Table 1).

3.3. FT-IR characterization of *β*-CDP

The FT-IR spectra of the β-CDPs crosslinked by citric acid were very similar to each other. The spectrum of A2, as a representative, was compared with the spectrum of native β-CD, as shown in

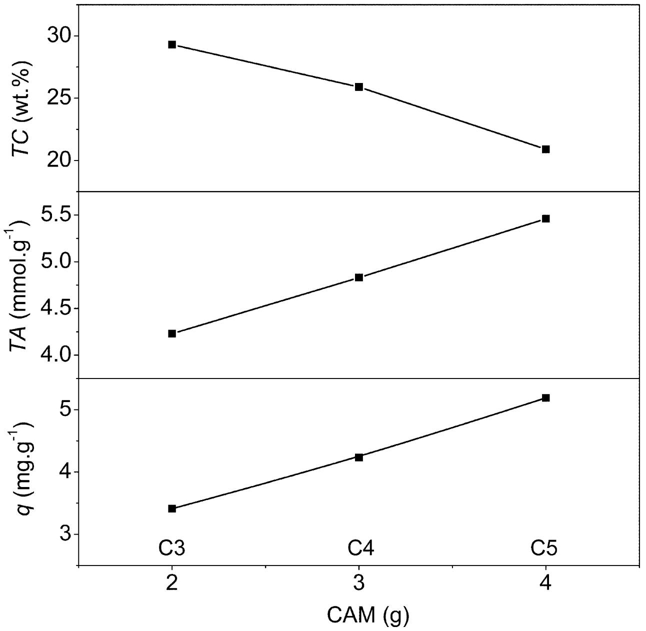

Fig. 4. *TC*, *TA* and *q* values of C3, C4 and C5 (*q* is the adsorption capacity toward aniline).

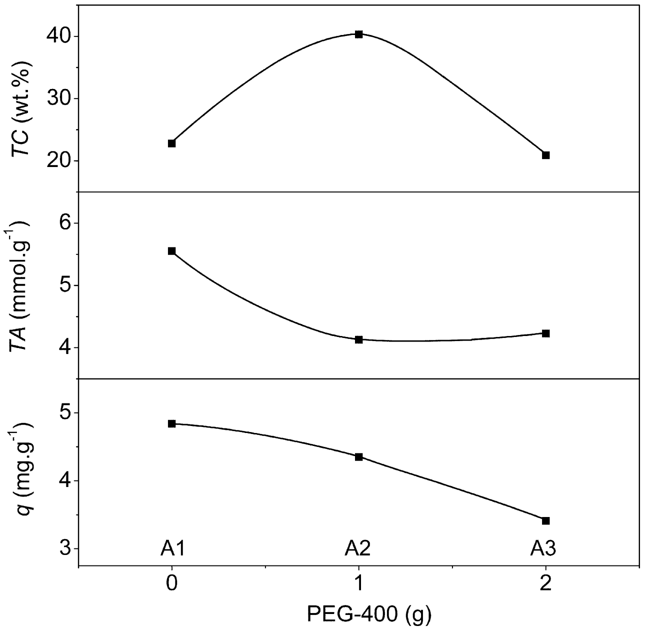

Fig. 5. *TC*, *TA* and *q* values of A1, A2 and A3.

Fig. 6. An intensive absorption band appeared at 1736 cm^{-1} in (b) which was absent in (a). This band was due to the C=O stretching vibration of ester groups and carboxyl groups in β-CDP. The peak at 1200 cm^{-1} in (b), which was also absent in (a), was owed to the C–O–C stretching vibration of ester groups. The absorption bands of ester groups observed in (b) indicated that the hydroxyl groups of β-CD had reacted with the carboxyl groups of citric acid and thereby a three-dimensional network was formed. Because of the crosslinked network, the β-CDP was stable and insoluble in water. The strong and broad band at 3400 cm^{-1} in (a) corresponded to the O–H stretching vibration of the hydroxyl groups in β-CD, and the similar band observed in (b) corresponded to the integrated O–H stretching vibration of the hydroxyl groups and carboxyl groups in β-CDP. The peaks at 2925 cm^{-1} in (a) and 2927 cm^{-1} in (b) corresponded to the CH_2 asymmetric stretching vibration. The C–OH stretching vibration at 1030 cm^{-1}, the C–O–C stretching vibration at 1159 cm^{-1}, and the other absorption bands including 1414 cm^{-1}, 947 cm^{-1}, 858 cm^{-1}, 756 cm^{-1} and 579 cm^{-1} in (a) for β-CD also appeared nearly at the same wavenumbers in (b) for β-CDP. It could be inferred that the structure characteristics of β-CD were well maintained in the β-CDP. The FT-IR spectra of citric acid and PEG-400 were compared well with A2 and the results also agreed with the above conclusions.

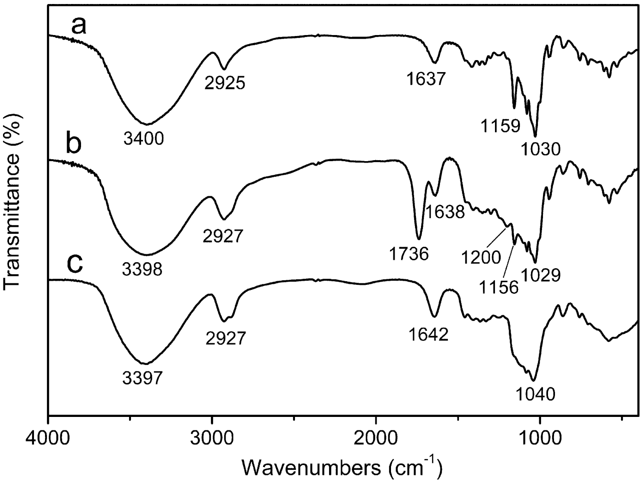

Fig. 6. FT-IR spectra of β-CD (a), A2 (b) and D1 (c).

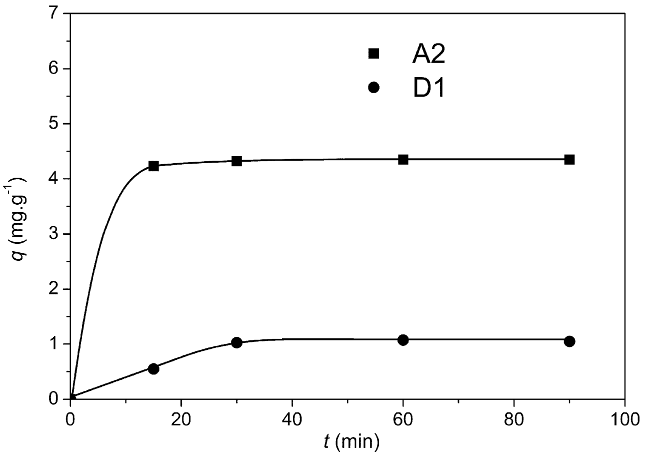

Fig. 7. Adsorption kinetics of aniline by A2 and D1 (C_0 = 54.9 mg L^{-1}).

3.4. Primary study on adsorption toward aniline by β-CDP

The produced β-CDPs were applied to adsorption experiments toward aniline which is a typical and hazardous pollutant in water (Environment Agency of UK, 2009). Aniline has one phenyl group and one amino group in its chemical structure. Phenyl group is a hydrophobic group which can be adsorbed by the hydrophobic cavity of β-CD. Amino group is a basic group which can react with carboxyl group. Thus, β-CD cavities and carboxyl groups in β-CDP can both contribute to adsorption toward aniline.

The adsorption capacity (q) toward aniline was found to be related to the *TA* of β-CDP. As shown in Fig. 4 (C3, C4 and C5), when β-CDP had a higher *TA*, it also had a higher q, although it had a lower *TC*. This indicated that acidic groups played an important role in the adsorption toward aniline. As shown in Fig. 5 (A1, A2 and A3), It's easy to understand that A1 had the largest *TA* and therefore the largest *q*. *TA* of A2 was almost equal to A3, but A2 had a much larger *q* than A3, probably because A2 had a much larger β-CD content (*TC*) which provided more opportunities for aniline to be captured by the cavities of β-CDs.

A comparative study was also performed between A2 and D1. D1 had no acidic groups since it was crosslinked by epichlorohydrin. As shown in Fig. 6, the absorption bands corresponding to acidic groups, which appeared in the FT-IR spectrum of A2, were absent in the spectrum of D1. The spectrum of D1 was quite similar to native β-CD, indicating that the structure characteristics of β-CD were well maintained in D1.

As shown in Fig. 7, D1 showed considerable adsorption toward aniline, indicating that β-CD cavities in D1 can adsorb aniline through hydrophobic interactions. A2 not only had a remarkably larger adsorption capacity ($q_e = 4.4\ \mathrm{mg\ g^{-1}}$) than D1 ($q_e = 1.1\ \mathrm{mg\ g^{-1}}$), but also had a much faster adsorption speed (t_e <15 min) than D1 ($t_e \approx$30 min). q_e and t_e represent equilibrium adsorption capacity and equilibrium time, respectively. This result again showed that the acidic groups in β-CDP were important for the adsorption toward aniline.

4. Conclusions

Water-insoluble β-cyclodextrin polymer (β-CDP) was synthesized by polycondensation using citric acid as crosslinking agent, sodium dihydrogen phosphate as catalyst and PEG-400 as modifier. A series of experiments disclosed that the yield (*Y*) of β-CDP was closely related with the amounts of citric acid, PEG-400 and catalyst in the formulation. β-CD content (*TC*) and total acidic groups (*TA*) of β-CDP were also found to be related to the formulation. Increase of citric acid in the formulation led to increase of *Y* and *TA* and decrease of *TC*. Suitable amount of PEG-400 led to the largest *Y* and *TC*, while excessive PEG-400 led to decrease of *Y* and *TC*. *Y* was considerably improved when sufficient catalyst was used, while too much catalyst was unnecessary. FT-IR spectra disclosed that the hydroxyl groups of β-CD had crosslinked with the carboxyl groups of citric acid, and at the same time the structure characteristics of β-CD were well maintained in β-CDP. The adsorption capacity (*q*) toward aniline was found to be related with *TA* of β-CDP. Generally, a larger *TA* resulted in a larger *q* toward aniline. β-CDP crosslinked by citric acid showed a much larger *q* than β-CDP crosslinked by epichlorohydrin, which again illustrated the importance of acidic groups in the adsorption toward aniline.

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