ORIGINAL ARTICLE

Synthesis of modified *β*-cyclodextrin polymers and characterization of their fuchsin adsorption

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Abstract Three water insoluble *β*-cyclodextrin polymers HP-*β*-CDP, CM-*β*-CDP and AE-*β*-CDP were synthesized by cross-linking epoxychloropropane with corresponding *β*-CD derivatives and utilized to adsorb water-soluble dye fuchsin from aqueous solution. FT-IR spectra confirmed the existence of hydroxypropyl, carboxyl group and amidogen in polymers. The influences of several parameters (contact time, pH and temperature) and the degree of substitution (DS) of CM-*β*-CDP in range of 1.5–4.5 on the adsorption capacity (Q_e) were evaluated. The results showed that all maximum Q_e of polymers appeared at pH 5.2–5.3. CM-*β*-CDP with carboxyl group was the most effective extractant, and the Q_e of CM-*β*-CDP with DS 1.5–2.5 kept nearly constant but decreased sharply over 2.5. However, AE-*β*-CDP with amidogen had displayed a quite low Q_e to fuchsin, even lower than that of unmodified *β*-CD polymer. The preliminary studies on the morphology of both CM-*β*-CDP and AE-*β*-CDP by AFM disclosed the differences in topography of their surfaces.

Keywords *β*-Cyclodextrin polymers · Water insoluble · Synthesis · Fuchsin · Adsorption

Introduction

Cyclodextrins(CDs) are a series of cyclicoligo-saccharides consisting of six to eight glucose units linked by α-(1 → 4) bonds. Possessing a toroid or hollow tapering cone with internal hydrophobic cavity, CDs have a remarkable capacity to form inclusion complexes with various molecules through host–guest interactions [1–4]. *β*-CD, the most largely produced cyclodextrin with seven glucose units, has been widely used in many fields such as pharmaceuticals, foods, and analytical methods [5–7]. Moreover, a large number of *β*-CD derivatives have been synthesized for improving their inclusion capacity by introducing various functional groups to help "catching" substrates [8–12]. However, the drawback of water solubility of *β*-CD and its derivatives limits their application for removal of organic pollutants and heavy metals from aqueous solution. To address the problem, water-insoluble cyclodextrin based polymers (*β*-CDPs) have been developed and become a new type of adsorbent useful for removal of organic pollutants and heavy metals in water [13–23].

In our previous study, we successfully synthesized *β*-CD polymer with hydroxypropyl which showed good adsorption capacity to phenol [24]. In this work, three water insoluble *β*-cyclodextrin polymers HP-*β*-CDP with nonionic hydroxy and CM-*β*-CDP with carboxyl group and AE-*β*-CDP with amidogen were synthesized and utilized to adsorb water-soluble dye fuchsin from aqueous solution. The purpose of this work was to investigate the influences of molecular structures on adsorption capacity including properties of functional groups and degree of substitution (DS) of carboxymethyl in CM-*β*-CDP. The chemical structures and composition of the polymers studied were shown in Fig. 1, and the synthetic route of *N*-(2-aminoethyl) amino dexoy-*β*-cyclodextrin crosslinked polymer (AE-*β*-CDP) in scheme 1.

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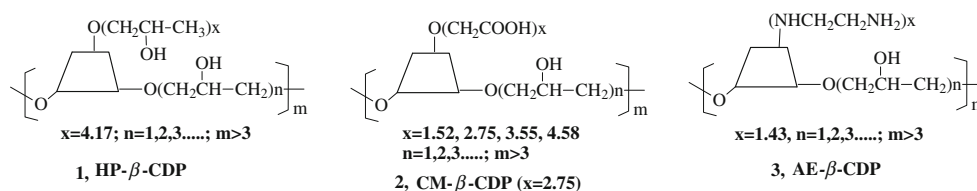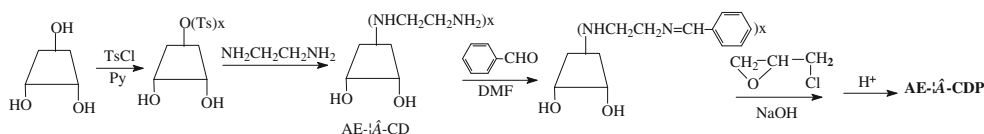e-mail: xmzhang6289@yahoo.com.cn

Fig. 1 Chemical structure of the polymers HP-β-CDP (1), CM-β-CDP (2) and AE-β-CDP (3) β-CD content (w/w): HP-β-CDP 58.6%, CM-β-CDP 58.3%, AE-β-CDP, 60.2%

Scheme 1 Synthetic route of N-(2-aminoethyl) amino dexoy-β-cyclodextrin polymer (AE-β-CDP)

Experimental

Reagents and solutions

β-Cyclodextrin, purchased from Anhui Shanhe Co., Ltd, China (puritiy ≥95.0%), was recrystallized by deionized water before use. Pyridine, analytical pure reagent purchased from guoyao Co., Ltd, was dried by potassium hydroxide over-night then redistilled before use. The analytical pure reagents ethylenediamine, toluene-p-sulfonyl chloride, epoxychloropropane, fuchsin, chloroacetic acid and sodium hydroxide were purchased from guaranteed manufacturers in China. All aqueous solutions were prepared with deionized water that had been passed through Ultrapure water system.

Apparatus

FT-IR spectra were recorded on a Bruker VECTOR 33FT-IR spectrometer using KBr pellets. ^{1}H NMR spectrum was obtained from a Bruker Avance 400 NMR spectrometer in deuterated water with TMS as internal standard. All the UV–Vis experiments were carried out using Bejing TU-1901 UV–Vis recording spectrophotometer. AFM imaging was carried out using AJ-III AFM (Ai Jian Nanometer Scientific Development Co., Ltd.) equipped with a 100 μm tripod scanner, in contact mode, using pyramidal cantilevers with silicon probe at a scan frequency of 1 Hz. Images processed with the SPMLab 5.01 soft ware package were presented unfiltered. HS-3C pH meter (Shang hai Precision Instrument Co., Ltd.) was used to measure the pH of solution.

Preparation of β-CD derivative monomers and polymers

Hydroxypropyl-β-CD polymer HP-β-CDP (1)

Monomer HP-β-CD with average degree of substitution (DS) 4.17 determined by ^{1}HNMR was prepared as previously described [25].

Monomer HP-β-CD (4.4 g) was dissolved in 30% (w/w) aqueous NaOH solution, followed by dropwise addition of epoxychloropropane (4.7 g) at 40 °C with stirring. Gel formed within 30 min and the reaction mixture was kept at 40 °C for 2 h to complete the reaction. The gel formed was washed with dilute hydrochloric acid and H$_2$O, dialyzed against H$_2$O to remove low molecular weight substances (≤3,500), followed by drying in vacuum oven at 80 °C and grind into 0.2 mm in diameter. Finally, 5.8 g polymer was obtained.

Carboxymethyl-β-CD polymer (CM-β-CDP) (2)

Monomer CM-β-CD was prepared by the reaction of β-CD with chloroacetic acid, and the DS of CM-β-CD was determined by typic non-aqueous titration method. The reactions of β-CD with chloroacetic acid at ratio of 1:3, 1:5, 1:7 and 1:9 (w/w) produced CM-β-CD with DS of 1.52, 2.75, 3.35, and 4.58, respectively.

Monomer CM-β-CD (4.2 g, DS 2.75) was dissolved in 30% (w/w) aqueous NaOH solution, followed by dropwise addition of epoxychloropropane (4.7 g) at 65 °C with stirring. Gel formed within 30 min and the reaction mixture was kept at 65 °C for 2 h to complete the reaction. The gel formed was washed with dilute hydrochloric acid and H$_2$O, dialyzed against H$_2$O to remove low molecular weight substances (≤3,500), followed by drying in vacuum oven at 80 °C and grind into 0.2 mm in diameter. Finally, 5.7 g polymer was obtained.

N-(2-aminoethyl) amino dexoxy-β-CD polymer (AE-β-CDP) (3)

Synthesis of AE-β-CD monomer

β-Cyclodextrin (10.0 g) was dissolved in dry Pyridine (40 mL), followed by dropwise addition of the solution of TsCl (7.0 g) in dry Pyridine (20 mL) at 5 °C with stirring. The resulting solution was stirred at 5 °C for 5 h and then

25 °C for 48 h. At end of this period, the product was precipitated by the addition of acetone and was filtered and washed by acetone. 3.2 g white powder TsO-β-CD was obtained after dried in vacuum oven.

A mixture of TsO-β-CD (5.0 g) in dry diaminoethane (40 mL) was stirred for 5 h at 70 °C under nitrogen. Excess diaminoethane was removed under reduced pressure then the product was precipitated by the addition of acetone. Filtered off and followed by drying in vacuum oven, 2.5 g light yellow powder AE-β-CD was obtained.

Synthesis of polymer AE-β-CDP

The DS of AE-β-CD, determined by typic non-aqueous titration method, was 1.43.

In a solution of AE-β-CD (4.0 g) in DMF (40 mL), glacial acetic acid was added to adjust the solution pH 4–5, then benzaldehyde (40 mL) was added. The mixture was stirred for 48 h at room temperature. At end of this period, the product was precipitated by the addition of acetone and was filtered and washed by acetone and ethanol. A yellow brown powder benzaldehyde AE-β-CD schiff base yielded after vacuum drying.

Benzaldehyde AE-β-CD schiff base (3.0 g) was dissolved in 20% (w/w) aqueous NaOH solution, followed by dropwise addition of epoxychloropropane (4.8 g) at 65 °C with stirring. Gel formed within 30 min and the reaction mixture was kept at 65 °C for 2 h to complete the reaction. Then, dilute hydrochloric acid (30 mL) was added and stirred for 12 h at 65 °C. The gel formed was dialyzed against H$_2$O to remove low molecular weight substances ($\leq$3,500), followed by drying in vacuum oven at 80 °C and grind into 0.2 mm in diameter. Finally, 3.7 g polymer was obtained.

β-CD polymer (β-CDP) (4)

β-cyclodextrin polymers was prepared as previously described in the synthesis of HP-β-CDP.

The β-CD contents (w/w) in polymers 1–4 were determined by the phenol–sulfuric acid method [26].

Adsorption experiments

The adsorption experiments were carried out using the aqueous solution of fuchsin. Fuchsin is a widely used dye with the structure of three aromatic rings combined to a carbon (see Fig. 2), which may be difficult to be adsorbed. Three β-CD polymers, containing nonionic hydroxy, carboxyl group and amidogen, respectively, synthesized by us were applied to adsorb fuchsin in water to evaluate their inclusion and adsorption properties. In order to calculate the concentration from each experiment, a calibration
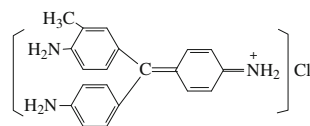

Fig. 2 Chemical structure of fuchsin

curve was first prepared. The calibration curve for aqueous solution of fuchsin was created by running different calibration standards (1, 2, 3, 4, 5 mg L^{-1}) at a certain pH (5.2 $\pm$ 0.1) to exclude the influence of pH to fuchsin itself. The absorbance values (A) were measured for each concentration (C) at λ_{max} 543 nm by UV–Vis spectrometer. The concentration (C) values were plotted against the corresponding A values and the data points were linearly fitted. The obtained calibration equation was: $A = 0.196\ 62\ C - 0.012\ 69$, $R = 0.995\ 8$. R was the correlation coefficient.

In each experiment, 0.1 g adsorbent was precisely weighed and put into a 50 mL conical flask which contained 25 mL fuchsin solution at a known concentration. The flask was well covered and then shaken in the water bath shaker according to the given condition. The pH of filtrate was adjusted to 5.2 $\pm$ 0.1, and then, the concentration of the solution was determined from the absorbance of the solution measured by the UV–Vis spectrophotometer. The experiments were performed twice under identical conditions.

The adsorption capacity of the adsorbent toward fuchsin was determined by the difference between the initial and remaining concentration of the fuchsin solution. The equilibrium adsorption capacity Q_e (mg g^{-1}) was calculated by:

$$Q_e = V(C_0 - C_e)/W \tag{1}$$

Where C_0 is the initial concentration (mg L^{-1}); C_e is the equilibrium concentration (mg L^{-1}); V is the volume of the solution used (L); and W is the weight of adsorbent used (g).

Results and discussion

Characterization of polymers

All three modified β-CD polymers (HP-β-CDP, CM-β-CDP and AE-β-CDP) and one unmodified β-CDP which acted as a contrast in the adsorption studies were water insoluble. The β-CD contents (w/w) in polymers were 58.6, 58.3, 60.2, and 61.5%, respectively.

Figure 3 was the FT-IR spectra of the synthesized HP-β-CDP(1), CM-β-CDP (2) and AE-β-CDP (3) compared with native β-CD (0). The absorption band at 1,384 cm^{-1} in (1)

Fig. 3 FT-IR spectra of HP-β-CDP (1), CM-β-CDP (2), AE-β-CDP (3) and β-CD (0)

was owed to C–H bent vibration of –CH$_3$, which was the evidence of hydroxypropyl in HP-β-CDP. The observable absorption band at 1,742 cm^{-1} in (2) which was absent in (1), (3) and (0) could be assigned as C=O stretching vibration of carboxyl groups in CM-β-CDP. The absorption band at 1,645 cm^{-1} in (3) was a combination of absorptions of H–O–H and H–N–H bent vibration in AE-β-CDP, and signal at 1,459 cm^{-1} corresponded to C–H bent vibration of >CH$_2$ in AE-β-CDP also. The strong and broad band at 3,388 cm^{-1} in (0) corresponded to O–H stretching vibration of the hydroxyl groups in β-CD, and the similar bands observed at 3,425 cm^{-1} in (1) corresponded to O–H stretching vibration of the hydroxyl group in HP-β-CDP, 3,423 cm^{-1} in (2) to the integrated O–H stretching vibration of the hydroxyl group and carboxyl group in CM-β-CDP and 3,417 cm^{-1} in (3) to the integrated O–H, N–H stretching vibration of the hydroxyl group and amidogen in AE-β-CDP. The C–H asymmetric stretching vibration of >CH$_2$ at 2,921 cm^{-1}, the C–OH stretching vibration at 1,030 cm^{-1}, and the other absorption bands including 1,158 and 578 cm^{-1} in (0) for β-CD

also appeared nearly at the same wave numbers in (1), (2) and (3), indicating that the structural characteristics of β-CD were essentially maintained in polymers.

Adsorption of fuchsin on polymers

Using three modified polymers (1, 2 and 3) and unmodified β-CDP 4 with β-CD contents within 58.3–61.5% as adsorbents, adsorption studies were carried out to examine the influence of various parameters such as adsorption rate (contact time), pH and adsorption temperature on the adsorption capacity Q_e of polymers 1, 2, 3, and those Q_e were compared with 4. The influence of DS of CM-β-CDP 2 on Q_e was also examined. The results showed that sorption of polymers to fuchsin in water took place easily, and could achieve adsorption equilibrium in 2–2.5 h.

Influence of pH on adsorption capacity

Due to acidic and basic functional groups containing in synthesized polymers, the charged species on polymers could be effected by pH, which would influence the inclusion of polymers to fuchsin in water. For example, –COOH in CM-β-CDP (p$K_a \approx 4$) would transform to negatively charged –COO$^-$ in alkaline medium, and –NH$_2$ (p$K_b \approx 3.5$) in AE-β-CDP would transform to positively charged –NH$_3^+$ in acidic medium. Moreover, there exist an amine salt group (=NH$_2^+$Cl$^-$, within pH 1.0–3.1) and two free aromatic amino groups (–NH$_2$) in fuchsin (see Fig. 2). The =NH$_2^+$ is becoming to imine group while pH is over 3.1, and fuchsin can be precipitated in NaOH solution. Therefore, the pH range for investigation was set within 2–11.

Figure 4 was the Q_e of polymers 1–4 versus pH. As shown in Fig. 4, polymers 1–4 possessed quite different
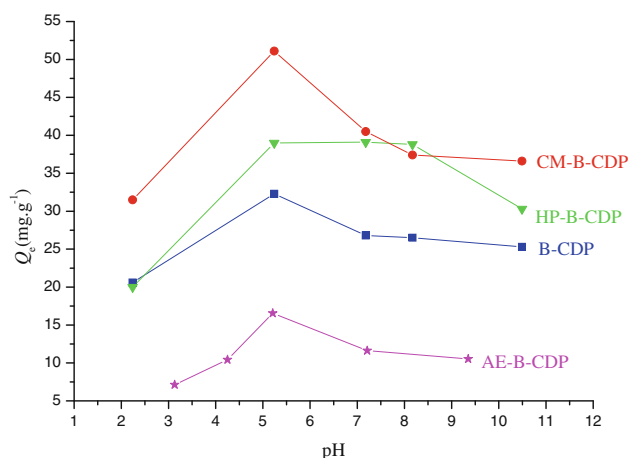

Fig. 4 Effect of pH on Q_e (Concentration of fuchsin 250 mg L^{-1}, 20 °C)

adsorption capacities on fuchsin, and pH affected the Q_e of them obviously within 2–11. All three maximum Q_e of polymers appeared at pH 5.2, which was 16.5 mg g^{-1} for AE-β-CDP, 32.3 mg g^{-1} for β-CDP and 39.0 mg g^{-1} for HP-β-CDP, and maximum Q_e of CM-β-CDP (54.6 mg g^{-1}) appeared at pH 5.3. In range of pH 2–11, fuchsin exists mainly in the form of positively charged =NH$_2^+$ in acidic medium (pH <3.1), and of electrically neutral imine group (=NH) in alkaline medium. Comparison with unmodified β-CD polymer, the fact that Q_e values of CM-β-CDP were evidently higher than those of others within pH 2–11 indicated the carboxyl group should be beneficial to β-CD units in CM-β-CDP for inclusion fuchsin. However, the Q_e values of AE-β-CDP were quite low, even lower than that of unmodified β-CDP and nonionic HP-β-CDP, though they possessed similar β-CD contents. This was mainly attributed to the influence of similar functional groups containing nitrogen in both AE-β-CDP and fuchsin which might present the same charged species in medium. Thus, inclusion process of positively charged AE-β-CDP (–NH$_3^+$) to positively charged fuchsin (=NH$_2^+$) wouldn't take place favorably due to electrostatic repellent in acidic medium; and the repellant interactions between groups containing nitrogen with lonely electron pair in both AE-β-CDP (–NH$_2$) and fuchsin (=NH, –NH$_2$) wouldn't do also in neutral or basic medium.

As for the maximum Q_e of polymers appearing at pH 5.2–5.3 and the similar Q_e trends to pH within 2–11, the conceivable reason might be attributed mainly to the change of the charged species of fuchsin with pH. Positively charged fuchsin (pH 2.0–3.1) would obstruct the inclusion process of polymers to fuchsin, and functional groups containing nitrogen (=NH, –NH$_2$, pH 7.0–11.0) with lonely electron pair did also. In the range of pH 3.1–7.0, positively charged =NH$_2^+$ began to transform to imine group =NH when pH increased, so fuchsin in water would exist in two forms,=NH$_2^+$ and =NH. The suitable ratio of =NH$_2^+$ and =NH at pH 5.2–5.3 might meet the optimal inclusion condition for polymers.

According to analysis above, it was supposed that the adsorption process of polymers to fuchsin should be the integrative effects of inclusion and various acting forces such as electrostatic and Vander Waals force.

Influence of temperature on adsorption capacity

Figure 5 was the influence of temperature on Q_e. As shown in Fig. 5, the Q_e of 1, 2 and 4 decreased slowly with the increase of temperature from 15 to 35 °C, which would mean the physical sorption between those polymers and fuchsin, but that of AE-β-CDP appeared a maximum at 25 °C. The maximum Q_e might be caused by the
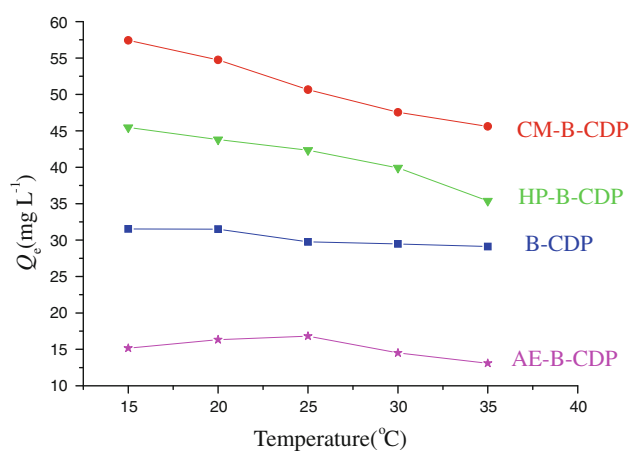

Fig. 5 Effect of temperature on Q_e. (Concentration of fuchsin 250 mg L^{-1}, pH 5.3)

interaction between functional groups containing nitrogen in adsorbate (=NH, –NH$_2$) and adsorbent (–NH$_2$).

Influence of DS of CM-β-CDP on Q_e

For seeking the effects of molecule structure on adsorption capacity, we investigated the changing of the Q_e of CM-β-CDP with DS in range of 1.5–4.5 (Fig. 6).

As shown in Fig. 6, Q_e decreased with the increase of DS from 1.5 to 4.5, and the similar trends were observed at different pH. Furthermore, Q_e declined slightly with the increase of DS from 1.5 to 2.5, but quickly when DS was over 2.5, especially at pH 5.4. The results could be explained in terms of the steric effect of multisubstituted carboxy methyl hindering the inclusion of CM-β-CDP to fuchsin. The lowest Q_e at pH 9.31 might be due to multi-negative charges of COO$^-$ on CM-β-CDP, which could act as an exemplification for the influence of multisubstituted
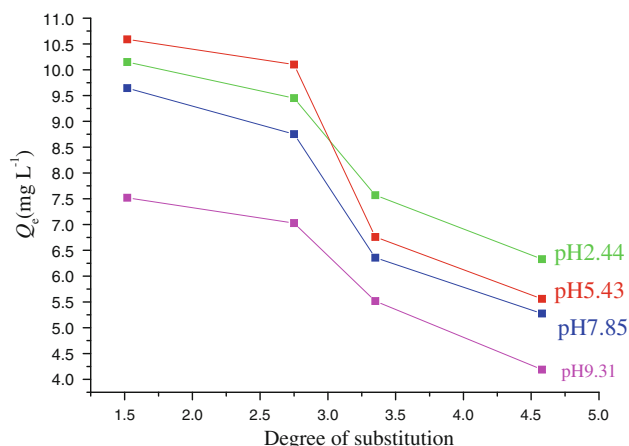

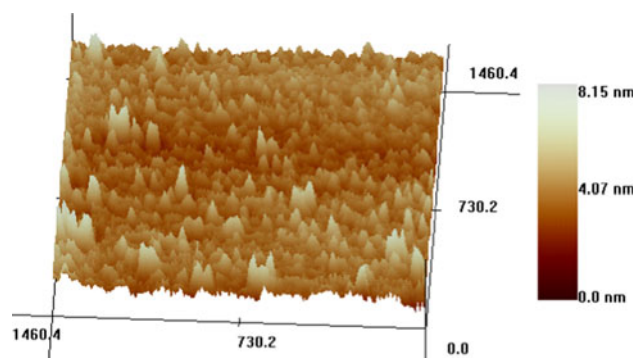**Fig. 6** Effect of degree of substitution of CM-β-CDP on Q_e. (Concentration of fuchsin 50 mg L^{-1}, 25 °C)

Fig. 7 Morphology of CM-β-CDP
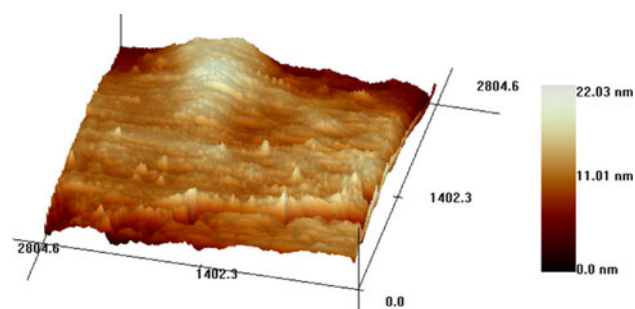

Fig. 8 Morphology of AE-β-CDP

groups on Q_e. Obviously, proper DS on CM-β-CDP should be one of important structural factors for getting efficient Q_e.

AFM of CM-β-CDP and AE-β-CDP

Considering the quite different Q_e between CM-β-CDP and AE-β-CDP with similar β-CD contents and particle size, the preliminary studies on the morphology of both CM-β-CDP and AE-β-CDP by AFM was carried out (Fig. 7, 8).

As shown in Fig. 7 and 8, both sample surfaces were irregular, and there were full of varisized dentations on the surface of CM-β-CDP while wavily dense papules on the surface of AE-β-CDP. The scraggly surface of CM-β-CDP could be favourable for fuchsin to approach to and be caught on adsorption sites. Further work concerning the influences of morphology on adsorption performances of the polymers has been in progress.

Conclusion

Three water insoluble β-cyclodextrin polymers HP-β-CDP, CM-β-CDP and AE-β-CDP were synthesized by cross-linking epoxychloropropane with corresponding β-CD derivatives. Their structures characterized by FT-IR spectra indicated the existence of hydroxypropyl, carboxymethyl

and amino in polymers. The fuchsin adsorption studies showed that the kinds of functional group on polymers influenced the adsorption capacity greatly, which CM-β-CDP (Q_e 54.6 mg g^{-1}) was the most effective extractant whereas the adsorption capacity of AE-β-CDP (Q_e 16.5 mg g^{-1}) was even lower than the unmodified β-CD polymer (Q_e 32.3 mg g^{-1}), and the Q_e of CM-β-CDP with DS 1.5–2.5 kept nearly constant but decreased sharply over 2.5. The adsorption process of polymers to fuchsin should be the integrative effects of inclusion and various acting forces such as electrostatic and Vander Waals force. It is believed that molecular designing for novel efficient adsorbents basen on β-CD polymers may benefit from our results.

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