

Preparation of Bimodal Porous Copolymer Containing β -Cyclodextrin and Its Inclusion Adsorption Behavior

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ABSTRACT: A novel insoluble bimodal porous polymer containing β -cyclodextrin (β -CD) was prepared to adsorb aromatic amine compound. The process involved copolymerization of styrene and methyl methacrylate with a maleic acid derivative of β -CD, subsequently, above formed copolymer was foamed by supercritical CO_2 . The chemical properties and physical structure of obtained copolymer was analyzed using Fourier transform infrared spectra, Thermal gravimetric analysis, X-ray diffraction, scanning electron microscope, and N_2 adsorption techniques. The inclusion adsorption of aromatic amine compounds on β -CD copolymer was carried out in a batch system. The quantities of aromatic amine compounds adsorbed on β -CD copolymer reached equilibrium within 60 min. The adsorption kinetic could be fitted to a pseudo-second-order kinetic equation, and the linear correlation coefficients varied from 0.9828 to 0.9935. With the influence of

molecular structure and hydrophobicity of the aromatic amine compound, the sequence of quantity of aromatic amine compounds adsorbed on β -CD copolymer is *p*-toluidine > aniline > benzidine > *o*-toluidine. The adsorption equilibrium data of aromatic amine compound adsorbed on β -CD copolymer were fitted to Freundlich and Langmuir models, respectively. The linear correlation coefficients of Langmuir model varied from 0.9516 to 0.9940, and the linear correlation coefficients of Freundlich varied from 0.9752 to 0.9976. It is concluded that Freundlich model fits better than Langmuir model, because the adsorption of aromatic amine compound on β -CD copolymer is a chemical process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2176–2185, 2010

Key words: β -cyclodextrin; bimodal porous copolymer; foaming; supercritical CO_2 ; inclusion adsorption

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides, consisting of glycopyranose units as a torus-like structure with hydrophilism on the outer surface and relative hydrophobicity in their internal cavity.^{1,2} The extraordinary structure of CD brings excellent adsorption properties to form inclusion complexes with guest molecules through a host–guest interaction.³ The driving force is the release of water from the cavity of cyclodextrin.⁴ Binding of guest molecules with cyclodextrin is a dynamic equilibrium and the corresponding equilibrium constant dictates the amount adsorbed.⁵ The main influence factor of complexation is dimensional fit between cavity and guest molecule.⁵ Besides, these cavities are shape and size selectivities, only molecules fits their dimensions can be adsorbed. As the hydrophobicity

varied for L-tryptophan, L-phenylalanine, and L-tyrosine, β -CD shows different adsorption quantities to each molecule.⁶

As CDs' solubility in water limits their applications to some extents, there have been considerable research interest on insoluble CD contained polymers.^{7,8} The technical route to prepare CD contained polymer focuses on either crosslinking of CD molecule with bifunctional agents,^{9,10} or immobilizing CD molecule as pendant units on polymer chains.^{11,12} Because CDs favor holding a guest molecule in their inner cavity,¹³ those CDs contained polymers are widely used in molecular recognition,¹⁴ separation,¹⁵ drug delivery,¹⁶ purification,¹⁷ and sensors.¹⁸

The procedure of adsorption by means of complexation includes three steps:¹⁹ first, the guest molecules diffuse from the solution to the polymer surface, second, the molecules diffuse through the boundary membrane to the entrance of the inner cavity of cyclodextrin, and finally, the molecules delivered from the outer to the interior of the cavities to form complex compound with cyclodextrin units of the polymer.

Maleic acid derivatives of β -CD (MACD) containing vinyl group are synthesized by reaction of

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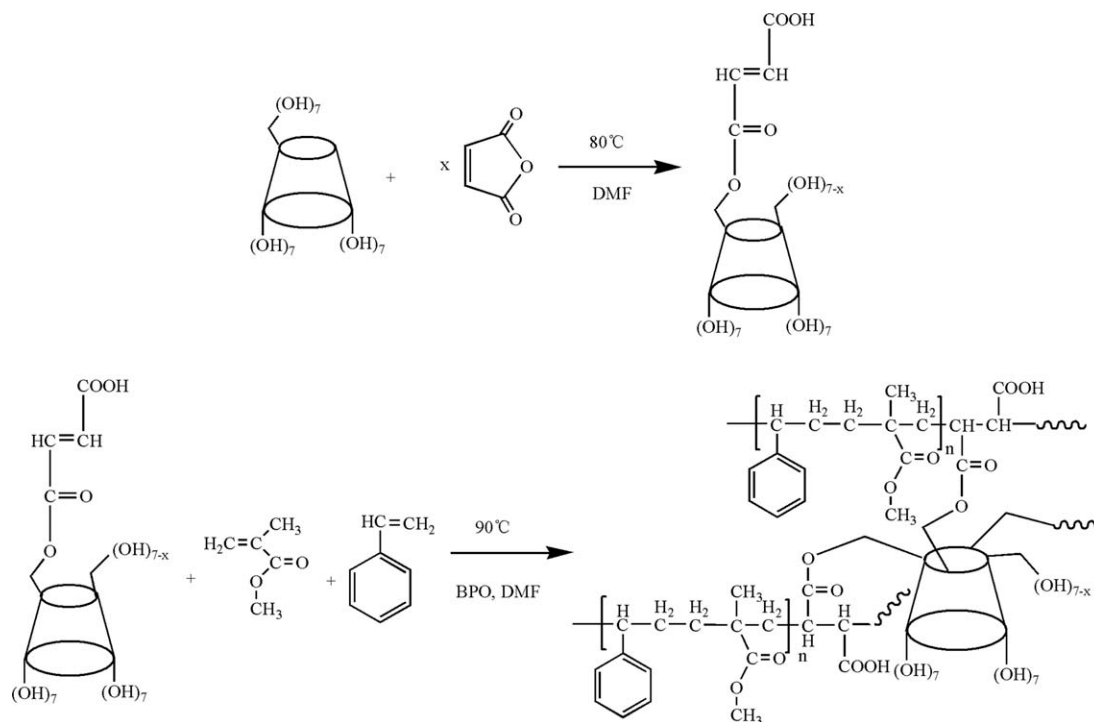


Figure 1 Preparation of β -CD copolymer.

β -cyclodextrin (β -CD) with maleic anhydride (MA) in dry dimethylformamide (DMF).²⁰ Further copolymerization of MACD with some vinyl monomers is a practical way to prepare β -CD polymer.²¹ Meanwhile, specific comonomers is chosen to tailor the properties of final polymer needed. Most of the β -CD units in β -CD copolymer are embedded in the bulk of the obtained polymer²² and are inaccessible to guests, which leads to a weak adsorption on the β -CD copolymer. Grinding the copolymer into fine powder can improve the inclusion behavior, however, result in difficulties in separation of the powder from the solution. To improve the availability of β -CD unit in β -CD copolymer, maximization of β -CD unit to surfaces is highly desirable. Therefore we develop here a new way to synthesize β -CD copolymer with high porosity.

The application of supercritical fluids (SCFs) have been widely studied for production of microporous polymers.²³ SCFs, in particular carbon dioxide, is very attractive owing to its extremely low level of toxicity and nonflammable nature.²⁴ Consequently, it is feasible to control the morphology of the polymer with supercritical CO_2 (sc CO_2).

Aromatic amine compounds are broadly employed in chemical industry, are thus frequently found in industrial waste water. Aromatic amine compounds can easily permeate through soil and contaminate ground water, so it is desired to remove them from waste water before release.²⁵ The diameter of β -CD internal cavity is about 0.60–0.65 nm,²⁶

in which the guest molecule with smaller diameter could be imbedded via noncovalent bonds.¹

In this article, we present the synthesis of a cyclodextrin derivative monomer and further radical copolymerization with styrene (STY) and methyl methacrylate (MMA). The synthesis route is shown in Figure 1. Subsequently, sc CO_2 was introduced to improve the porosity of the obtained polymer. We also exhibit the application of those polymers on inclusion adsorption of various aromatic amine compounds, which are known to be harmful to both environment and our human body. The results demonstrated remarkable performance of this copolymer in inclusion adsorption.

EXPERIMENTAL

Materials

Chemical grade β -CD (Guoyao Chemical Reagent Co., Shanghai, China) was recrystallized twice from aqueous solution, filtrated, and dried under vacuum at 110°C over 12 h prior to use. MA was purchased from Lingfeng Chemical Reagent Co., Shanghai, China, and was used without further purification. MMA and STY of analytical grade (Lingfeng Chemical Reagent Co., Ltd, Shanghai, China) were further purified with 5% NaOH to remove the inhibitor followed by washing with deionized water till pH = 7 and are dried over night with Na_2SO_4 . Finally, distilled under reduced pressure and stored at 0°C for

use. Benzoperoxide (BPO, Guoyao Chemical Reagent Co., Shanghai, China) was recrystallized from methanol and dried under vacuum at ambient temperature. DMF of analytical reagent (Shanghai Chemical Reagent Co., Shanghai, China) was dried by molecular sieve (4A) for 12 h. Molecular sieve (4A) calcinated at 350°C before use was bought from Guoyao Chemical Reagent Co., Shanghai, China. Other chemical reagents were used without further purification.

Techniques

Fourier transform infrared (FTIR) spectra were taken with KBr pellets on a Nicolet-5700 spectrophotometer from Thermo Electron Corporation America. Thermal gravimetric analysis (TG) was carried out by SDT Q600 thermogravimetric analyzer from TA America, each sample was run from 50 to 800°C at a scan rate of 10°C min⁻¹ under nitrogen atmosphere. X-ray diffraction (XRD) was performed on a D/MAX 2550 VB/PC diffractometer from Rigaku Japan over the range of 3–50°. The morphology of the β-CD copolymer before and after scCO₂ foaming was investigated by a JSM-6360LV scanning electron microscope (SEM) from Jeol Japan. BET N₂ adsorption was detected by ASAP 2010 from Micromeritics America. Ultraviolet-visible spectra were taken by UV-7504 spectrophotometer from Xinmao, Shanghai, China. A SHA-C constant temperature water bath oscillator from Anpu (Shanghai, China) was used for batch inclusion adsorption. Materials Studios software was provided by state key lab of chemical engineering, East China University of Science and Technology.

Preparation and inclusion adsorption

Synthesis of MACD

MACD was synthesized according to the procedures described elsewhere.²⁷ A certain amount of β-CD (5.0 g, 4.4053 mmol) and MA (6.0 g, 61.1870 mmol) were dissolved in 30 mL of DMF in a round-bottom flask. The mixture was allowed to react under stirring at 80°C for 12 h. When the reaction was completed, the solution was cooled to room temperature and slowly poured into 200 mL of ethyl acetate. The obtained precipitate was recovered by filtration and dried at 80°C under 0.005 MPa for 24 h. The mass of obtained MACD did not change at 16 and 20 h, we are convinced that the reaction were finished after 12 h.

Copolymerization of MACD with MMA and STY

A certain amount of MACD (7.0 g) was dissolved in 30 mL of DMF, then MMA (8 mL) and STY (8 mL) were added. The mixture was bubbled with nitrogen for 40 min before radical polymerization was carried out with 0.5 wt % benzoperoxide as initiator at 90°C

for 12 h. Once the reaction was completed, the mixture was poured into 200 mL of methanol and the precipitate was filtered. The obtained product was dried at 80°C under 0.005 MPa for 24 h.

Foaming of β-CD contained copolymer with scCO₂

A 50 mL stainless steel vessel equipped with accurate pressure gauge was used for scCO₂ processing. After charging 4.0 g β-CD copolymer in the vessel, the temperature and pressure were raised to 60°C and 15 MPa. When the pressure was stabilized, the impregnation of the polymer finished. Ultimately, the pressure of the vessel was vented to ambient conditions within one second.

Inclusion adsorption

Inclusion adsorption of aromatic amine compounds on β-CD copolymer in aqueous solution was conducted batchwise. The effect of inclusion adsorption time was followed to determine kinetic model of aromatic amine compound inclusion adsorption and equilibrium time. The kinetic study was obtained by determine the concentration of the mixture of 0.5 g of β-CD copolymer with 25 mL of aromatic amine compound solutions with initial concentration of 100 mg/L at different intervals. Adsorption equilibrium isotherm was obtained by mixing 0.5 g of β-CD copolymer with 25 mL of aromatic amine compound solutions with initial concentration from 5 to 100 mg/L. The mixture was shaken at a rate of 220 rpm at 25°C.

The experimental value of equilibrium adsorbed quantity (Q_e) of aromatic amine compounds on β-CD copolymer obtained from experimental data was calculated by eq. (1).

$$Q_e = \frac{V \times (c_i - c_e)}{m_s} \quad (1)$$

Where c_i and c_e are the initial and the equilibrium concentration of aromatic amine compound expressed in mg/L, respectively; V is the volume of aromatic amine compound solution expressed in L; m_s is the mass of β-CD copolymer expressed in g; Q_e is expressed in mg/g.

The distribution coefficient (R_d)²⁸ could be determined by eq. (2).

$$R_d = \frac{\text{mass of aromatic compound in adsorbent}}{\text{mass of aromatic compound in solution}} \times \frac{V}{m_s} = \frac{Q_e}{c_e} \quad (2)$$

Analytical method

A UV-7504 spectrophotometer was used to determine the concentration of aromatic amine

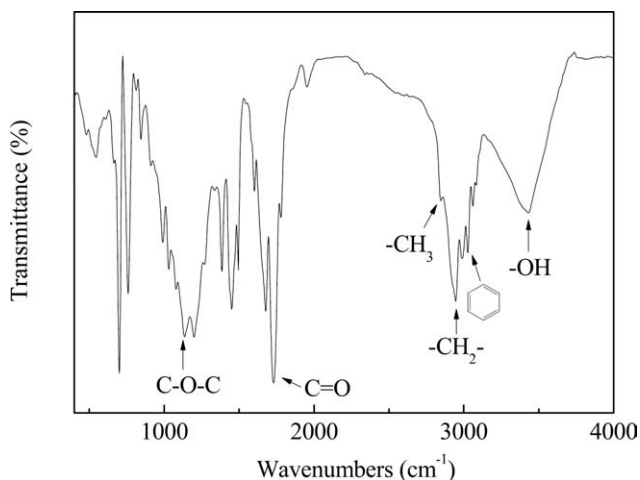


Figure 2 FTIR characterization of β -CD copolymer.

compounds before and after inclusion adsorption. Preparation of standard curve was conducted according to a procedure reported previously.²⁹ The method is based on aromatic amine compound could react with nitrite and *N*-(1-naphthyl)ethylenediamine dihydrochloride to form amaranth dyes, which have the largest absorbance at 545 nm. Briefly, 10 mL of a solution containing each aromatic amine was adjusted to pH 1.5–2.0 with KH_2PO_4 solution (10 wt %). Subsequently, a drop of NaNO_2 solution (5 wt %) was added. After 3 min, the solution was mixed with 0.5 mL of ammonium sulfamate solution (2.5 wt %). After 3 min, 1 mL of *N*-(1-Naphthyl)ethylenediamine dihydrochloride is added. The solution was kept at 26°C for 30 min and measured at 545 nm.

RESULTS AND DISCUSSION

Fourier transform infrared spectra of β -CD copolymer

The obtained β -CD copolymer was determined through FTIR. Figure 2 shows the FTIR pattern of the obtained β -CD copolymer. It is clearly observed that there is a characteristic peak of α -pyranil vibration of β -CD at 942 cm^{-1} . Characteristic peaks of C—O—C that observed at 1199 and 1136 cm^{-1} are from MMA and MACD. The peaks at 1730 and 1779 cm^{-1} belonging to the C=O group originate from MMA and MA, respectively. The signals at 2946 and 2988 cm^{-1} are from the skeleton CH_2 group and CH_3 group, respectively. Aromatic C—H stretching vibration at 3026, 3060, 3082 cm^{-1} belong to the phenyl ring. The peak at 3430 cm^{-1} is result from —OH group on the β -CD.³⁰ It can be concluded that the polymer we got is copolymerized from MACD, MMA, and STY.

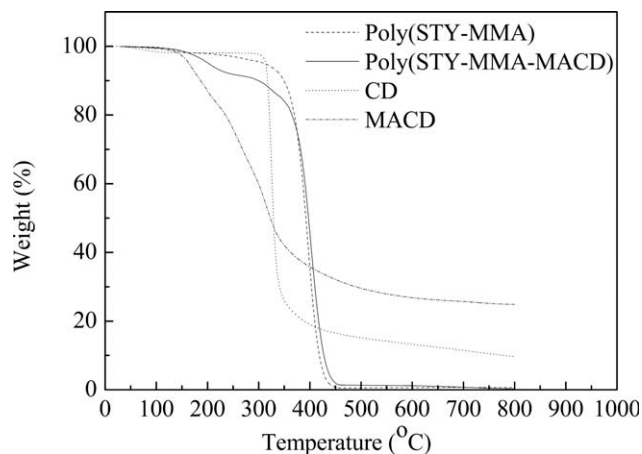


Figure 3 TG characterizations of β -CD and its derivative.

Thermal gravimetric analysis of β -CD copolymer

The TG curve of β -CD, MACD, poly(STY-MMA), and poly(STY-MMA-MACD) were shown in Figure 3. Poly(STY-MMA) is copolymerized by 8 mL of STY and 8 mL of MMA under exactly the same condition as preparation of poly(STY-MMA-MACD). Compared with the curve of MACD, the weight loss of poly(STY-MMA-MACD) that begins at 160°C is attributed to the decomposition of MACD. Compared with the curve of β -CD, the second weight loss at about 300°C is designated to degradation of the β -CD molecule. With respect to the curve of poly(STY-MMA), a weight loss at about 350°C is from thermal decomposition of the poly(STY-MMA).

X-ray diffraction pattern of β -CD copolymer

Figure 4 indicates the XRD curve of β -CD copolymer. An evident broadening peak ranging from 6 to 38° centered at 17° is observed, which reveals the amorphous patterns of the β -CD copolymer. The

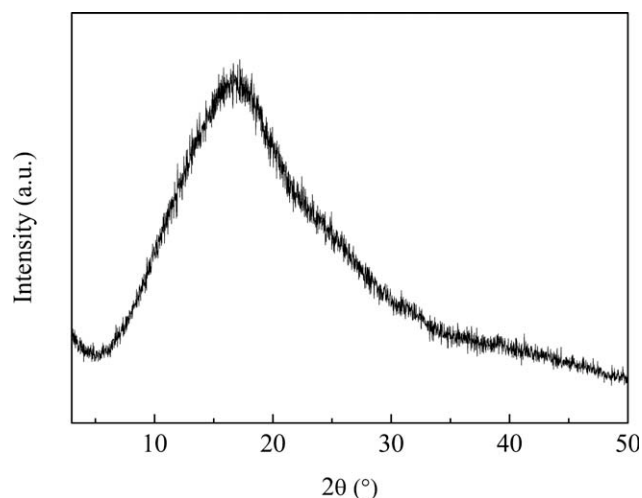


Figure 4 XRD characterization of β -CD copolymer.

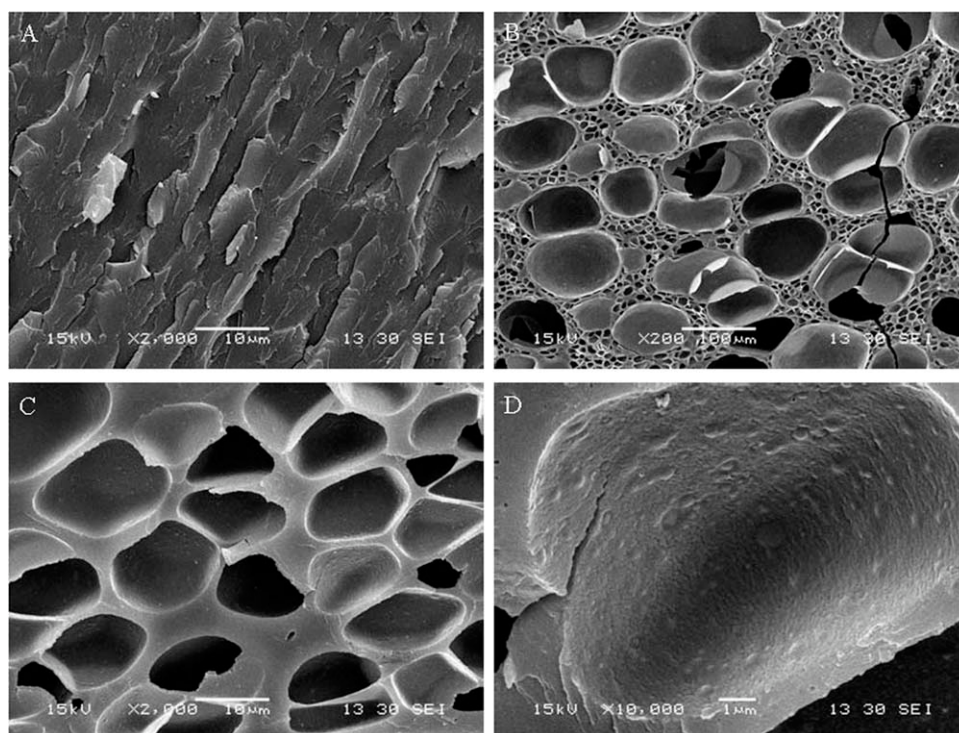


Figure 5 SEM images of nonfoamed (A) and foamed (B, C, and D) β -CD copolymer.

amorphous patterns are supposed to be caused by high crosslinking between MACD, MMA, and STY. As there are 21 hydroxyl groups on a β -CD molecule, more than one vinyl group will be immobilized on β -CD when MA reacted with β -CD. Meanwhile, there will be more than one branched chain on a β -CD molecule, that means the whole structure of obtained β -CD copolymer is high crosslinked structure.

Scanning electron microscopy of β -CD copolymer

The β -CD copolymer before and after $scCO_2$ treatment were shown in Figure 5. In Figure 5(B), it is evident that the foamed polymer possessing bimodal pores larger than $100\ \mu\text{m}$ and smaller holes about $10\ \mu\text{m}$ was obtained. Figure 5(C,D) is the SEM images of smaller holes with different magnifications. The bimodal porous structure should be caused by the solubility of $scCO_2$ in different area. $scCO_2$ has much higher solubility and diffusivity in polymers.³¹ When $scCO_2$ diffused into the β -CD copolymer, the space between each β -CD copolymer chains were swelled. The swelling were determined by the solubility of $scCO_2$ in β -CD copolymer. When the pressure was quenched to atmospheric conditions at $15\ \text{MPa/s}$ in one second, the diameter of holes in area with higher solubility of $scCO_2$ was bigger than the area with lower solubility of $scCO_2$. Meanwhile, the BET surface area of nonfoamed β -CD copolymer is $0.75\ \text{m}^2/\text{g}$ and the BET surface

area of foamed β -CD copolymer is $0.87\ \text{m}^2/\text{g}$. The surface area did not show evident difference is resulted from the closed-cell morphology of foamed copolymer.

Adsorption of aromatic amine compounds

Figure 6 shows the effect of inclusion adsorption time on the quantities of different aromatic amine compounds adsorbed by nonfoamed β -CD copolymer. Q_t (mg/g) is the quantity of aromatic amine compounds adsorbed on β -CD copolymer at time t .

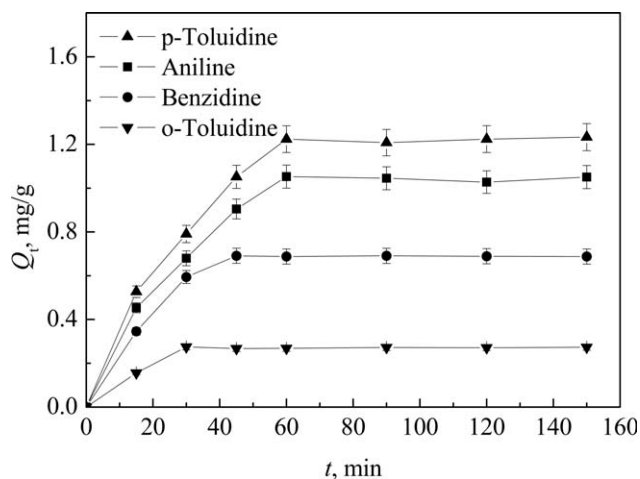


Figure 6 Effect of inclusion adsorption time on quantity of aromatic amine compounds adsorbed by nonfoamed β -CD copolymer.

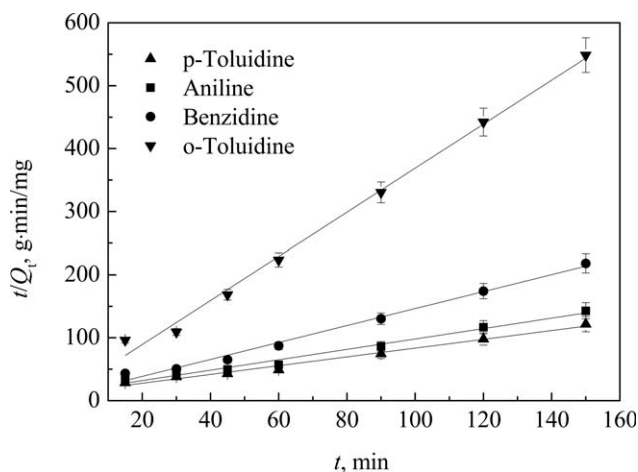


Figure 7 Pseudo-second-order model of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer.

The quantities of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer enhance with inclusion adsorption time and acquire equilibrium within 60 min. Consequently, 120 min of inclusion adsorption time was used for the next equilibrium experiments. Pseudo-second-order model³² was applied to analyze the kinetics behavior of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer. The form of pseudo-second-order model is shown in eq. (3)

$$\frac{t}{Q_t} = \frac{1}{k_s Q_m^2} + \frac{1}{Q_m} t \quad (3)$$

Where, Q_m (mg/g) is the calculated value of equilibrium adsorbed quantity of aromatic amine compound on β -CD copolymer, k_s is pseudo-second-order rate constant. Q_m and k_s can be calculated from the intercept and slope by plotting of t/Q_t versus t (Fig. 7). The value of Q_m and k_s are listed in Table I.

The linear correlation coefficients (R^2) ranging from 0.9828 to 0.9935 indicates that the pseudo-second-order model agreed well with inclusion adsorption of aromatic amine compounds on nonfoamed β -CD copolymer for the whole adsorption period. Simultaneously, Q_e , which is obtained in experiments and is also listed in Table I is close to Q_m . This kinetic behavior of aromatic amine compounds

adsorbed on nonfoamed β -CD copolymer reveals that the rate-determining step may be chemical adsorption.³³ This confirms that adsorption of aromatic amine compound takes place via complexation until the cavities of cyclodextrin units are fully occupied.

Figures 8 and 9 display the adsorption equilibrium isotherm of aromatic amine compounds adsorbed on β -CD copolymer at initial solution concentration of 5–100 mg/L. With the increasing of the equilibrium concentration, the quantity adsorbed on β -CD copolymer was also raised. It can be concluded that the aromatic amine compound molecules with higher concentration favor complexing with β -CD unit.

Moreover, at the same equilibrium concentration, the quantities of aromatic amine compounds adsorbed on β -CD copolymer are different. The main influence of complexation between aromatic amine compounds and β -CD molecule is the molecular structure and hydrophobicity of aromatic amine compounds.³⁴ The characteristics of aromatic amine compounds molecule are shown in Table II. The dipole moment of the molecules was referred from bibliography³⁵ and the structure size was calculated through Materials Studios software. Referring to the dipole moment of these aromatic amine compounds, the sequence of hydrophobicity between these aromatic amine compounds is *o*-toluidine < *p*-toluidine < aniline < benzidine. As *o*-toluidine molecule is big in size and weak in hydrophobicity than the rest of aromatic amine compounds, its quantity adsorbed on β -CD copolymer is the lowest among others. Although benzidine is the most hydrophobic of all aromatic amine compounds, the amino groups on the two ends of benzidine molecule are hydrophilic. The hydrophilicity hinders the benzidine molecule from accessing the inner cavity of β -CD molecule. This can be the reason that the quantity of benzidine adsorbed on β -CD copolymer is lower than *p*-toluidine and aniline. Meanwhile, minding the structure size and shape of *p*-toluidine and aniline, the aniline molecule is shorter than the β -CD cavity with a depth of 0.79 nm. Then *p*-toluidine molecule is more suitable to the β -CD cavity than aniline molecule and more stable complex are formed between β -CD and *p*-toluidine. Consequently, the quantity of aniline adsorbed on β -CD copolymer was smaller than

TABLE I
Pseudo-Second-Order Model Parameters for Aromatic Amine Compounds Adsorbed on Nonfoamed β -CD Copolymer

Adsorbate	k_s , g/(mg min)	Q_m (mg/g)	R^2	Q_e (mg/g)
Aniline	0.09491 \pm 0.0049	1.209 \pm 0.062	0.9828	1.0536
Benzidine	0.04727 \pm 0.037	0.742 \pm 0.03	0.9892	0.8467
<i>p</i> -Toluidine	0.1490 \pm 0.0034	1.432 \pm 0.07	0.9846	1.2521
<i>o</i> -Toluidine	0.00423 \pm 0.19	0.286 \pm 0.009	0.9935	0.4656

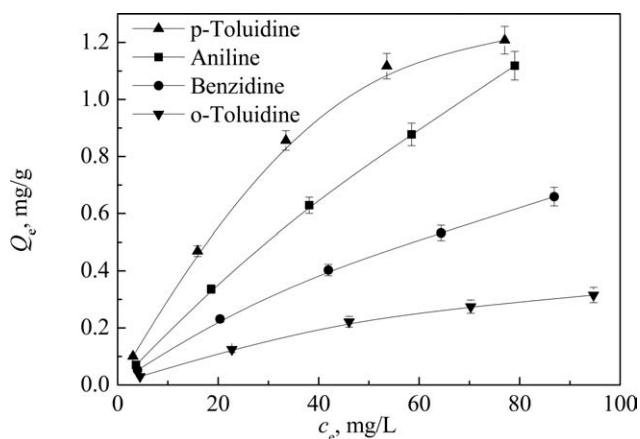


Figure 8 Adsorption equilibrium isotherms of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer.

p-toluidine. It can be concluded that the molecular size plays an important role compared to molecular polarity during the complexation. Ultimately, the sequence of quantity adsorbed on β -CD copolymer is *p*-toluidine > aniline > benzidine > *o*-toluidine.

Comparing the amount of aromatic amine compounds adsorbed on β -CD copolymer before and after scCO_2 processing at the initial concentration of 100 mg/L, the foamed β -CD copolymer has higher adsorbability on benzidine and *o*-toluidine of 0.1875 and 0.1502 mg/g than nonfoamed β -CD copolymer. Meanwhile, the foaming procedure has no effect on the sorption of *p*-toluidine and aniline. The scCO_2 processing seems to be less effective in improving the adsorption ability of organic compounds. The probable reason behind is that the closed-cell structure of the foamed β -CD copolymer is still not open to guest molecules even after scCO_2 treatment. Based on this observation, we prepared a kind of

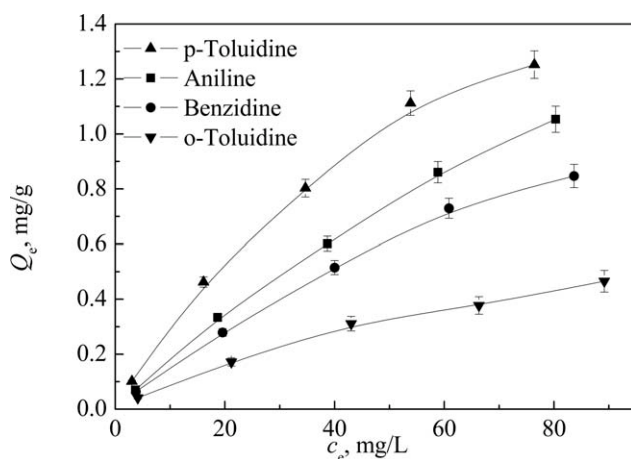


Figure 9 Adsorption equilibrium isotherms of aromatic amine compounds adsorbed on scCO_2 foamed β -CD copolymer.

TABLE II
Characteristics of Aromatic Amine Compound Molecule

Aromatic amine compounds	Dipole moment (D)	Width (nm)	Length (nm)
<i>p</i> -Toluidine	1.52	0.4335	0.6495
Aniline	1.13	0.4328	0.5635
Benzidine	0	0.4320	1.0677
<i>o</i> -Toluidine	1.60	0.5638	0.5602

β -CD copolymer with open-cell structure in next experiment.

Figures 10 and 11 indicate the influence of initial aromatic amine compounds concentration on their distribution coefficient. The R_d decreased with an increment in the initial concentration of all aromatic amine compounds because limited inclusion adsorption sites on the β -CD copolymer. Consequently, there may be no sufficient β -CD unit to accommodate aromatic amine compound molecules to be adsorbed on β -CD copolymer.

To optimize the adsorption procedure of aromatic amine compounds on β -CD copolymer, Langmuir and Freundlich adsorption isotherms are introduced to describe the interaction between aromatic amine compounds and β -CD copolymer. The data of equilibrium adsorbed quantities on β -CD copolymer and equilibrium concentrations in solution of aromatic amine compounds are employed from Figures 8 and 9.

The Langmuir sorption isotherm³⁶ is expressed in linear form of eq. (4)

$$\frac{c_e}{Q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} c_e \quad (4)$$

Where K_L (L/g) and a_L (L/mg) are the Langmuir isotherm constants, the value of which could be obtained from the intercept and slope by plotting of

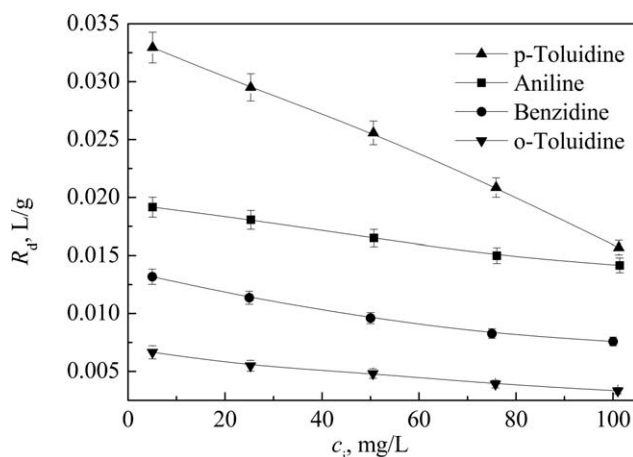


Figure 10 Influence of initial concentration on R_d of the inclusion adsorption on nonfoamed β -CD copolymer.

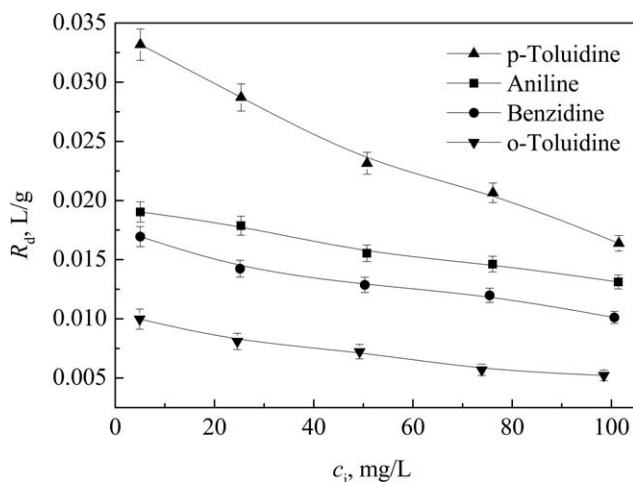


Figure 11 Influence of initial concentration on R_d of the inclusion adsorption on $scCO_2$ foamed β -CD copolymer.

c_e/Q_e versus c_e . The Langmuir sorption isotherm can be evaluated by separation factor (R_L)³⁷ which is formulated by eq. (5).

$$R_L = \frac{1}{1 + a_L c_i} \quad (5)$$

$R_L > 1$ means unfavorable adsorption property, $0 < R_L < 1$ means favorable adsorption property, $R_L=0$ means irreversible and $R_L = 1$ means linear adsorption property.³⁸

Figures 12 and 13 portray Langmuir isotherms of aromatic amine compounds adsorbed on β -CD copolymer before and after $scCO_2$ foaming, and the Langmuir constants are shown in Table III. R^2 varying from 0.9516 to 0.9940 indicates that the Langmuir isotherm equation is in agreement with inclusion adsorption of aromatic amine compounds on β -CD copolymer.

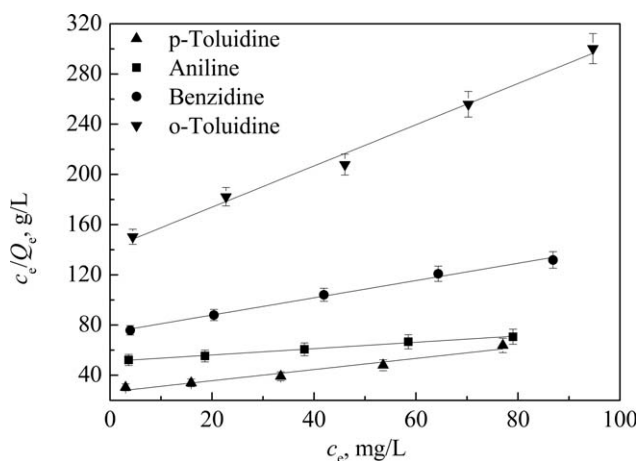


Figure 12 Langmuir isotherms of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer.

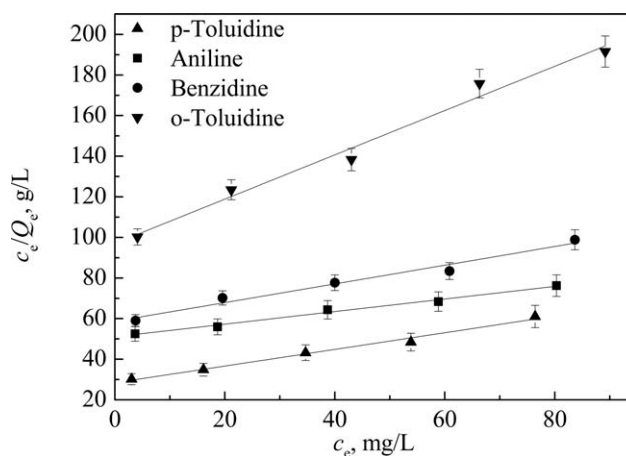


Figure 13 Langmuir isotherms of aromatic amine compounds adsorbed on $scCO_2$ foamed β -CD copolymer.

The values of R_L for aromatic amine compounds adsorbed on β -CD copolymer before and after $scCO_2$ foaming are displayed in Figures 14 and 15. The calculated R_L values range from 0.3730 to 0.9755, which implicating that the favorable inclusion adsorption of aromatic amine compounds on β -CD copolymer. The values decreased with an enhancement in the initial aromatic amine compound concentration is on account of the inclusion adsorption procedure had a higher adsorption efficiency at lower concentration.³⁹

The Freundlich sorption isotherm⁴⁰ is expressed in linear form of eq. (6)

$$\log Q_e = \log K_F + \frac{1}{n_F} \log c_e \quad (6)$$

K_F and n_F are Freundlich isotherm constants, the value of which could be obtained from the intercept and slope by plotting of $\log Q_e$ versus $\log c_e$. K_F is related to the adsorption capacity, meanwhile n_F is depend on the energy or intensity of the adsorption and reveals the favorability of the adsorption procedure.⁴¹ According to previous theory,³⁹ $n_F = 1$ represents the adsorption is linear, $n_F > 1$ represents the adsorption is a chemical process and $n_F < 1$ represents the adsorption is a favorable physical process.

Figures 16 and 17 exhibit Freundlich isotherms of aromatic amine compounds adsorbed on β -CD copolymer before and after $scCO_2$ foaming, and the Freundlich constants are shown in Table IV. The linear correlation coefficients of Langmuir model varied from 0.9516 to 0.9940, which are bigger than the linear correlation coefficients of Freundlich varied from 0.9752 to 0.9976. It can be concluded that the Freundlich isotherm gives a better fitting than the Langmuir isotherm. As the value of n_F ranges from 1.1053 to 1.2666, the inclusion adsorption is confirmed as a chemical process.

TABLE III
Constants Obtained from the Langmuir Isotherms Reported in Figures 12 and 13

Adsorbate	Adsorbent	K_L (L/g)	a_L (L/mg)	R^2
Aniline	Nonfoamed β -CD copolymer	0.01958 ± 0.00018	0.004958 ± 0.00014	0.9940
	Foamed β -CD copolymer	0.01958 ± 0.00032	0.006061 ± 0.00024	0.9871
Benzidine	Nonfoamed β -CD copolymer	0.01348 ± 0.00029	0.009283 ± 0.00021	0.9920
	Foamed β -CD copolymer	0.01704 ± 0.0006	0.007852 ± 0.00042	0.9666
<i>p</i> -Toluidine	Nonfoamed β -CD copolymer	0.03738 ± 0.0029	0.01661 ± 0.00043	0.9516
	Foamed β -CD copolymer	0.03520 ± 0.00136	0.01446 ± 0.0003	0.9851
<i>o</i> -Toluidine	Nonfoamed β -CD copolymer	0.007087 ± 0.00024	0.011631 ± 0.00019	0.9896
	Foamed β -CD copolymer	0.01030 ± 0.00045	0.01124 ± 0.00032	0.9779

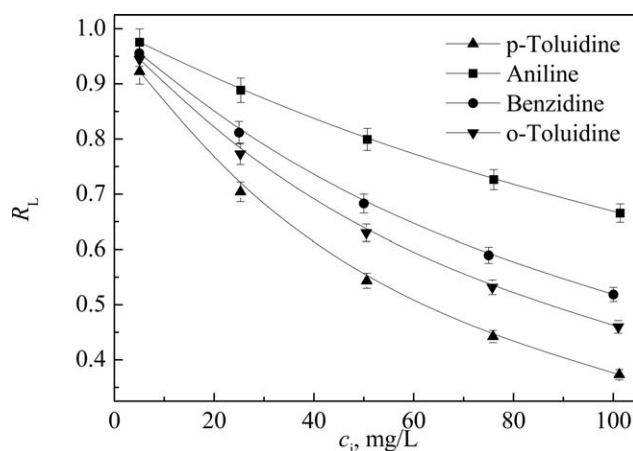


Figure 14 Separation factor for aromatic amine compounds adsorbed on nonfoamed β -CD copolymer.

CONCLUSIONS

An insoluble β -CD containing polymer was prepared by copolymerization of STY, MMA, and MACD. Further foaming treatment in $scCO_2$ create the bimodal porous structure of obtained copolymer. The structures of these polymers are characterized

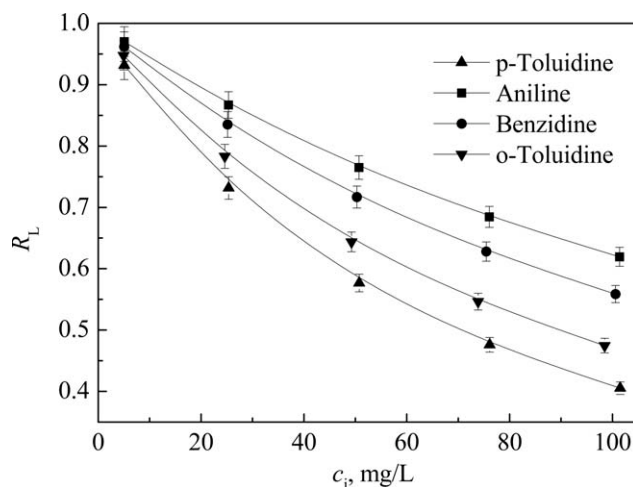


Figure 15 Separation factor for aromatic amine compounds adsorbed on $scCO_2$ foamed β -CD copolymer.

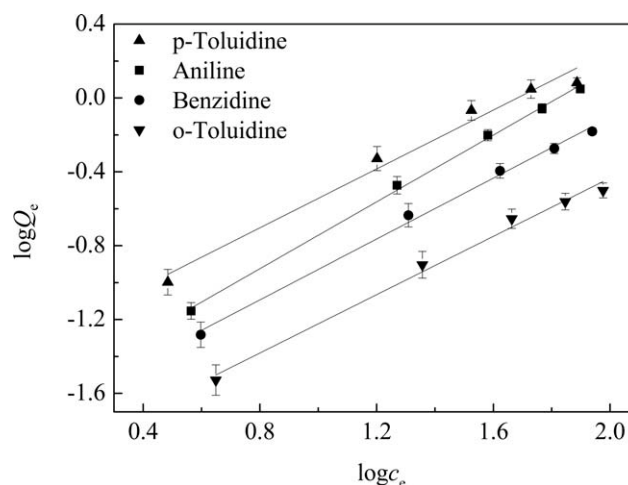


Figure 16 Freundlich isotherms of aromatic amine compounds adsorbed on nonfoamed β -CD copolymer.

by FTIR, TG, XRD, SEM, and N_2 adsorption techniques. Kinetic and equilibrium studies of aromatic amine compounds adsorbed on β -CD copolymer were conducted in aqueous solutions. The maximum adsorption capacity was obtained in 60 min, while the pseudo-second-order model reveals that the rate-

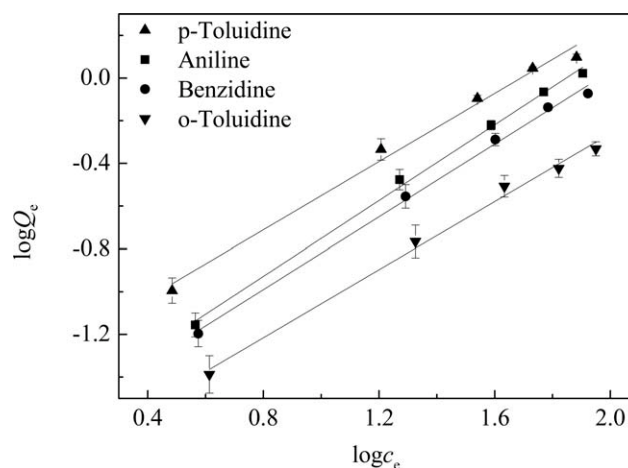


Figure 17 Freundlich isotherms of aromatic amine compounds adsorbed on $scCO_2$ foamed β -CD copolymer.

TABLE IV
 Constants Obtained from the Freundlich Isotherms Reported in Figures 16 and 17

Adsorbate	Adsorbent	K_F	n_F	R^2
Aniline	Nonfoamed β -CD copolymer	0.02247 ± 0.0064	1.1053 ± 0.026	0.9976
	Foamed β -CD copolymer	0.02303 ± 0.0079	1.1280 ± 0.033	0.9964
Benzidine	Nonfoamed β -CD copolymer	0.01766 ± 0.0083	1.2133 ± 0.044	0.9945
	Foamed β -CD copolymer	0.02131 ± 0.0078	1.1747 ± 0.036	0.9960
<i>p</i> -Toluidine	Nonfoamed β -CD copolymer	0.04561 ± 0.025	1.2546 ± 0.092	0.9752
	Foamed β -CD copolymer	0.04471 ± 0.018	1.2523 ± 0.067	0.9873
<i>o</i> -Toluidine	Nonfoamed β -CD copolymer	0.009710 ± 0.0097	1.2666 ± 0.068	0.9874
	Foamed β -CD copolymer	0.01404 ± 0.0096	1.2561 ± 0.057	0.9908

determining step is the chemical adsorption. Various molecular structure and hydrophobicity made the sequence of quantity of aromatic amine compound adsorbed on β -CD copolymer is *p*-toluidine > aniline > benzidine > *o*-toluidine. Langmuir and Freundlich model were both used to describe the inclusion adsorption procedure, and the linear correlation coefficients of Langmuir model varied from 0.9516 to 0.9940 and the linear correlation coefficients of Freundlich varied from 0.9752 to 0.9976. It can be concluded that Freundlich model gives a better fitting than the other one. The value of $n_F > 1$ manifests the inclusion adsorption of aromatic amine compound on β -CD copolymer is a chemical process.

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