

Equilibrium of Benzidine Inclusion Adsorption on Cyclodextrin Copolymer

Zhao-Yang Sun,¹ Gui-Ping Cao,¹ Hui Lv,¹ Ling Zhao,¹ Tao Liu,¹ Ludovic Montastruc,² Nikov Jordan²

¹UNILAB, State Laboratory of Chemical Engineering, Ecust China University of Science and Technology, Shanghai 200237, China

²Laboratoire ProBioGEM EA 1026, Ecole Polytechnique Universitaire de Lille, Université des Sciences and Technologies de Lille, France

Received 3 July 2008; accepted 11 January 2009

DOI 10.1002/app.30017

Published online 18 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Insoluble β -cyclodextrin (β -CD) copolymer was prepared by reacting β -CD with hexamethylene diisocyanate, and its inclusion adsorption behavior was investigated. The physical and chemical properties of CD copolymer were characterized by SEM, FTIR, DSC, TGA, XRD, and BET N₂ adsorption. The effects that shaking time and temperature exerted on the inclusion adsorption of benzidine on CD copolymer have been studied at relative low

initial benzidine concentration. The procedure of the inclusion adsorption could be described by the Freundlich equation, and the thermodynamic constants ΔH^\ominus , ΔS^\ominus and ΔG^\ominus were obtained simultaneously. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3882–3888, 2009

Key words: β -cyclodextrin copolymer; inclusion adsorption; benzidine; equilibrium

INTRODUCTION

Cyclodextrins (CDs) are a group of cyclic oligosaccharides composed of α -1,4-D-glucopyranose units.¹ The CD molecule has a torus-like structure with hydrophilic hydroxyl groups on the outer surface and relative hydrophobicity in the internal cavity.² Consequently, it is capable of forming inclusion complexes with hydrophobic compounds.³ Considering their unique inclusion adsorption ability, CD could be used to form specific inclusion complexes with organic compounds, such as aromatic compounds.⁴ The stability of such a guest–host complex depends on the hydrophobicity of the guest molecule and how the guest molecule fits into the central cavity of CD.⁵ Owing to the inclusion complexation characteristics, CD and its derivatives are applicable to a variety of areas, such as molecular recognition,⁶ artificial enzyme,⁷ drug delivery,⁸ recovery,⁹ and sensors.¹⁰

As CD is soluble in water, its application is limited. Therefore, many methods were investigated to prepare CD polymer.¹¹ However, only a few have been reported concerning inclusion adsorption behavior of

organics on CD polymer as a guest molecule.¹² Benzidine is widely used in the chemical industry as a dye-stuff; as a result, it is often observed in effluent water. Due to its high polarity and high solubility in water, benzidine would easily permeate through soil and contaminate ground water.¹³ The diameter of β -CD internal cavity is about 0.60–0.65 nm,¹⁴ whereas the breadth of the benzidine molecule is about 0.43 nm, in which the benzidine molecule can be imbedded via noncovalent bonds.¹⁵

In this paper, insoluble CD copolymer was prepared, and the inclusion adsorption behavior was studied. The inclusion adsorption of benzidine from water samples for CD copolymer were evaluated and compared with activated carbon. Static adsorption experiments exhibited specific ability of the CD copolymer on inclusion complex formation. The adsorption mechanism of benzidine on CD copolymer was also studied.

EXPERIMENTAL

Materials

β -CD of chemical grade (Guoyao Chemical Reagent, Shanghai, China) was recrystallized twice from water and dried under vacuum at 110°C for 12 h before use. Dimethyl formamide (DMF) of analytical reagent (Shanghai Chemical Reagent, Shanghai, China) was dried by a molecular sieve (4 Å) for 12 h. Hexamethylene diisocyanate (HMDI, 99% pure) was obtained from Sigma-Aldrich (Milwaukee, WI).

Correspondence to: G.-P. Cao (gpcao@ecust.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20490204, 20676031, 20876051.

Contract grant sponsor: Science and Technology Commission of Shanghai Municipality; contract grant number: 0552nm039.

Benzidine of analytical reagent was obtained from Yuanhang Chemical Reagent (Shanghai, China). Other chemical reagents were used without further purification.

Instrument

Elemental analysis was carried out by using Elementar Analysensysteme (Germany). Scanning electron microscope (SEM) was recorded from Jeol (Japan). X-ray diffraction was carried out by Rigaku (Japan). Fourier Transform Infrared spectroscopy was detected by Magna-IR 550 from Nicolet America. BET N₂ adsorption was detected by ASAP 2010 from America. Ultraviolet (UV)-Visible Spectrophotometer from Unico was used for recording UV spectra. Thermal Gravimetric Analysis (TGA) was carried out from TA America.

Preparation of CD copolymer

β -CD copolymer was synthesized by reacting β -CD with HMDI in dried DMF.¹⁵ A total of 3 g (2.643×10^{-3} mol) of β -CD was dissolved in 85 mL of DMF in a 250-mL, round-bottom flask at room temperature. Then, 3.30 mL (20.428×10^{-3} mol) of HMDI was added dropwise. After that, the solution was stirred at 80°C for 32 h under N₂ protection until HMDI disappeared. The CD copolymer was precipitated in a beaker with 300 mL methanol. The copolymer was recovered by filtration and dried under 0.01 MPa at 80°C for 24 h. Subsequently the CD copolymer was stirred in deionized water until the absorbance of deionized water in spectrophotometer at 545 nm was 0. Finally, the copolymer was dried under 0.01 MPa at 110°C for 12 h.

Characterizations of CD copolymers

In order to determine the physical and chemical properties of CD copolymer, various characterization methods were used. Elementar Vario EL III was chosen to make an elemental analysis of the CD copolymer to get the mass fraction of N element (p_N) in the CD copolymer. The content of CD in the CD copolymer (c_{CD}) was calculated by using the following equation:

$$c_{CD} = \frac{1 - \frac{p_N}{14} \times 0.5 \times 168.2}{1134.8} \quad (1)$$

where c_{CD} is expressed in mol/g.

The heating rate of TGA was 10°C/min from ambient to 800°C. Differential Scanning Calorimetry (DSC) was carried out with a heating rate of 10°C/min in the temperature range of 50–350°C. BET N₂ adsorption was degassed 6 h and analyzed at 77 K.

Adsorption method

Inclusion adsorption of benzidine with CD copolymer was researched batchwise. Then, 25 mL benzidine solution was mixed with 50 mg of the CD copolymer and shaken for 1 h at a speed of 230 rpm under the temperature over the range of 283–353 K. Adsorption equilibrium isotherm was obtained with initial benzidine concentration from 1 to 100 μ g/mL. UV-vis spectrophotometer was used to determine the concentration of benzidine after adsorption. Preparation of standard curve was conducted according to a procedure reported previously.¹⁶

The equilibrium adsorbed quantity of benzidine (Q_e) on CD copolymer is calculated as:

$$Q_e = \frac{V \times (c_i - c_e)}{m_s} \quad (2)$$

where c_i is initial concentration of the benzidine solution expressed in mol/L; c_e is equilibrium concentration of the benzidine solution expressed in mmol/L; V is the volume of benzidine solution expressed in L; m_s is the mass of CD copolymer expressed in g; and Q_e is expressed in mol/g.

RESULTS AND DISCUSSION

Preparation and characterization of CD copolymer

Fourier transform infrared (FTIR) was used to confirm whether the reaction completed.

Figure 1 shows the FTIR spectra of the reaction system before and after reaction. The peak at 2270 cm^{-1} corresponding to isocyanate group shown in (a) had disappeared in (c) and (d), indicating that HMDI was

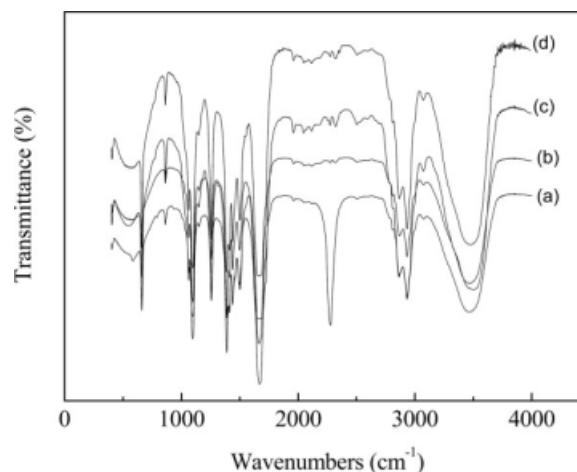


Figure 1 FTIR spectra of the solution before and after reaction. (a) The mixture before reaction, including HMDI, DMF, and CD. (b) The mixture of DMF and CD. (c) The system after reaction with the mole ratio of $n_{CD}/n_{HMDI} = 1 : 8.5$. (d) The system after reaction with the mole ratio of $n_{CD}/n_{HMDI} = 1 : 7.8$.

TABLE I
Synthesis of CD Copolymer at 80°C in DMF for 30 h

No.	n_{CD} (mmol) ^a	n_{HMDI} (mmol)	p_N	$c_{\text{CD}} \times 10^3$ (mol/g)
1	2.3774	20.5024	0.0917	0.3957
2	2.6484	20.5024	0.0898	0.4058

^a n_{CD} and n_{HMDI} are the molar weight of CD and HMDI added into flask, respectively.

entirely reacted. On one CD molecule, there are 21 hydroxyl groups, which can be divided into three categories equally based on the differences of their reactivity. Take (c) for example: the mole ratio of HMDI to CD in reaction was 8.5 : 1, and the mole ratio of —NCO to —OH was 17 : 21, which means all of those 21 hydroxyl groups on the CD could react with HMDI.

The analytical result of CD copolymer is summarized in Table I.

Figure 2 shows the FTIR spectra of CD copolymer (a) and CD (b). Comparing with the spectrum of CD, the growth of the vibration bands at 3370 cm^{-1} corresponded to the N—H group. The growth of the vibration bands at 1715 cm^{-1} represented the C=O group. The growth of the vibration bands at 1530 cm^{-1} corresponded to the NH—CO groups. All of those peaks proved that a new polymer was formed.

Figure 3 shows the SEMs of the CD copolymer. The morphology of the microcosmic structure was observed.

The BET surface area of CD copolymer is 5.4391 m^2/g . As such low surface area of the CD copolymer, we can conclude that the adsorption mechanism of the CD copolymer is different from physical adsorption.

Figure 4 shows the TGA curve of CD and CD copolymer. Two different temperature regions of weight loss were observed in the curve of CD copolymer, whereas there is only one on CD curve. Compar-

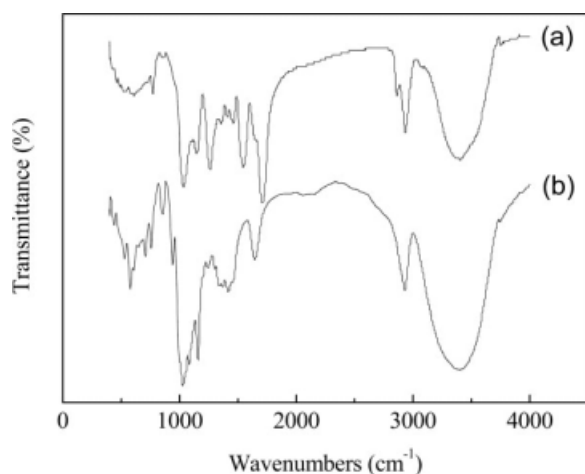


Figure 2 FTIR spectra of CD copolymer (a) and CD (b).

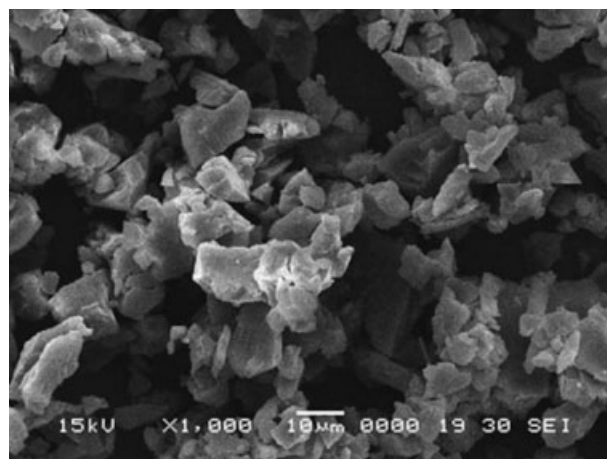


Figure 3 SEM of the CD copolymer ($\times 1000$).

ing with the curve of CD, the first region of the weight loss at about 300°C could be considered as degradation of the CD molecule. The weight loss at about 450°C should be due to the decomposition of carbamide linkages.

Figure 5 displays the DSC curve of CD copolymer. The observed glass-transition temperature of the CD copolymer is 103°C. The absence of melting peak may be due to amorphous pattern of the CD copolymer. Related with TGA curve, it can be concluded that the exothermic peak around 330°C was caused by the decomposition of the material.

Figure 6 indicates the X-ray diffraction (XRD) curve of CD copolymer. An evident peak was observed at 20°C, which revealed the amorphous patterns of the CD copolymer. The amorphous patterns were caused by highly crosslinking between CD and HMDI.

Inclusion adsorption of benzidine

β -CD has an internal diameter of 0.60–0.65 nm and depth of 0.79 nm,¹⁴ whereas the breadth and length

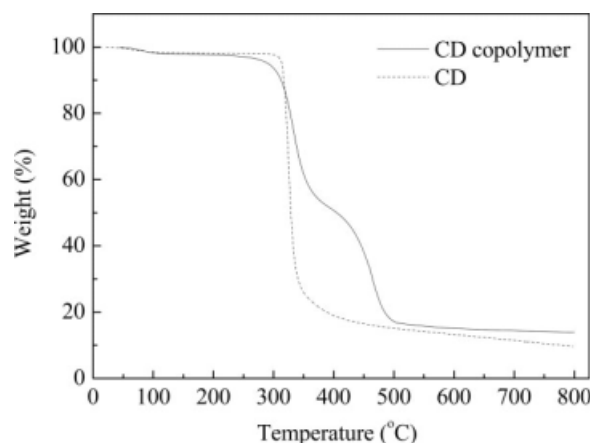


Figure 4 The TGA curve of CD and CD copolymer.

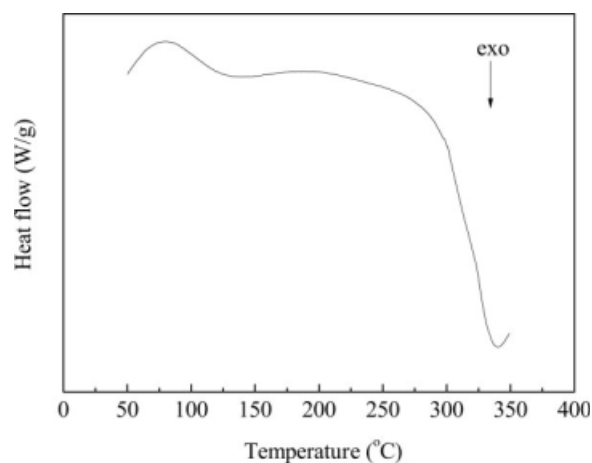


Figure 5 The DSC curve of CD copolymer.

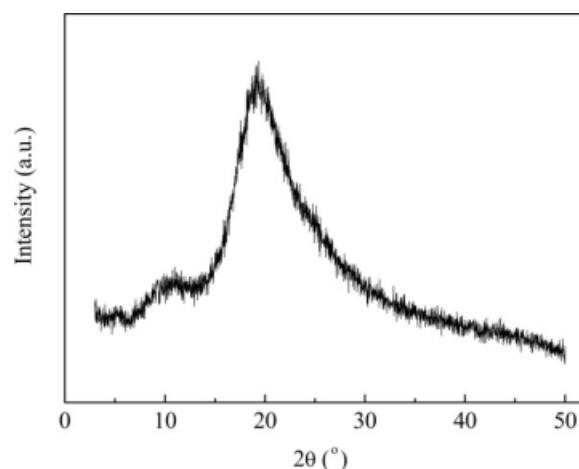


Figure 6 The XRD curve of CD copolymer.

of the benzidine is about 0.429 nm and 1.071 nm (calculated with Materials Studios software). Thus, the procedure of the inclusion adsorption could be expressed as in Figure 7.

The adsorption of benzidine on CD copolymer is affected by temperature, initial concentration of benzidine solution, and shaking time between solid and liquid phase. The adsorbability of activated carbon was also studied for comparison.

Figure 8 indicates the influence of shaking time on the adsorption of benzidine solution using 0.05 g of sorbent and 25 mL of 0.028 mmol/mL initial benzidine concentration at pH = 7 and 298 K. Compared with activated carbon, lower equilibrium concentration and less equilibrium time were observed in CD copolymer. The equilibrium concentration from CD copolymer was 0.005 mmol/L, which was lower than that of activated carbon. The CD copolymer reached equilibrium within less than 2 min, whereas activated carbon needed about 30 min. The average inclusion adsorption rate of CD copolymer is 5.9902

$\times 10^{-6}$ mmol/(s m²), which is much larger than that of activated carbon of 2.1721×10^{-9} mmol/(s m²).

Figure 9 exhibits the effect of temperature on the equilibrium adsorption quantity of benzidine on CD copolymer over the temperature range of 283–353 K at an initial solution concentration of 0.5428 mmol/mL, 0.050 g CD copolymer, 60 min shaking time at pH = 7, and 230 rpm shaking speed. A noticeable decrease in equilibrium adsorption quantity was observed with the increase in temperature, which means lower temperature is better for inclusion adsorption.

Figure 10 reveals the adsorption equilibrium isotherm of benzidine adsorbed on CD copolymer over the temperature range of 283–353 K at an initial solution concentration of 1–100 μ g/mL, 0.050 g CD copolymer, 60 min shaking time at pH = 7, and 230 rpm shaking speed. As the equilibrium concentration was increased, the quantity adsorbed on CD copolymer was also increased. That means that the benzidine molecule with higher concentration will

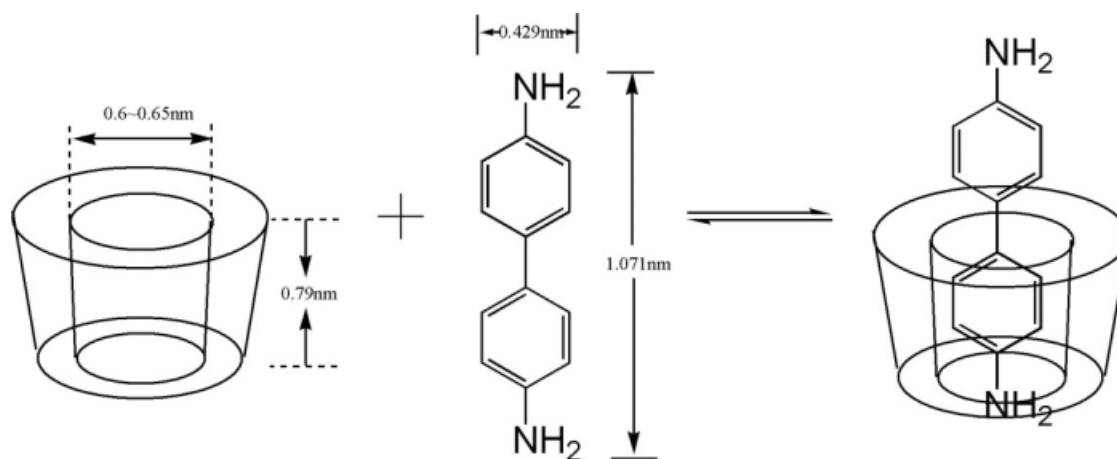


Figure 7 Inclusion complex of benzidine with CD copolymer.

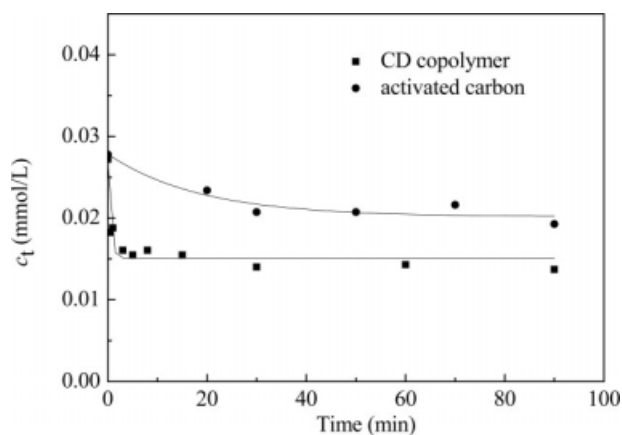


Figure 8 Influence of shaking time on the concentration of benzidine solution using CD copolymer and activated carbon.

have more probability to come into contact with the CD internal cavity.

The Freundlich adsorption isotherm¹⁷ gives an empirical expression encompassing the surface heterogeneity and the exponential distribution of energies, expressed with the following equation:

$$Q_e = K_f c_e^{1/n} \quad (3)$$

where Q_e is the amount of benzidine adsorbed per unit mass of CD copolymer at equilibrium (mol/g); c_e is the equilibrium concentration of benzidine in the solution (mol/L); and K_f and n are empirical constants dependent on the nature of sorbent and solute and temperature. By taking logarithms of both sides of eq. (3), we obtain

$$\log Q_e = \log K_f + \frac{1}{n} \log c_e \quad (4)$$

Plotting of $\log Q_e$ versus $\log c_e$ should be linear with slope equals to $1/n$ and intercept equals to \log

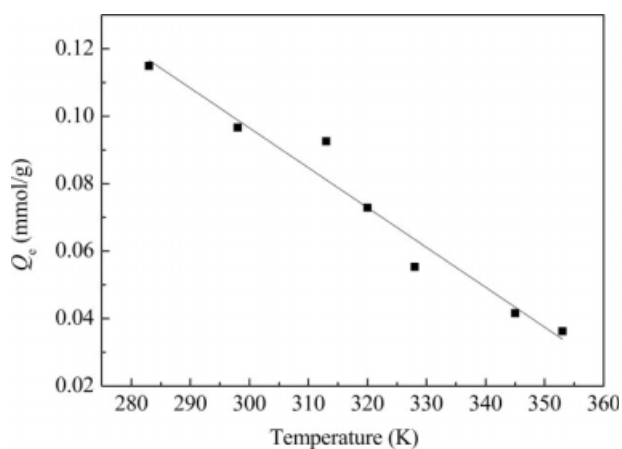


Figure 9 Effect of temperature on equilibrium adsorption quantity of benzidine on CD copolymer.

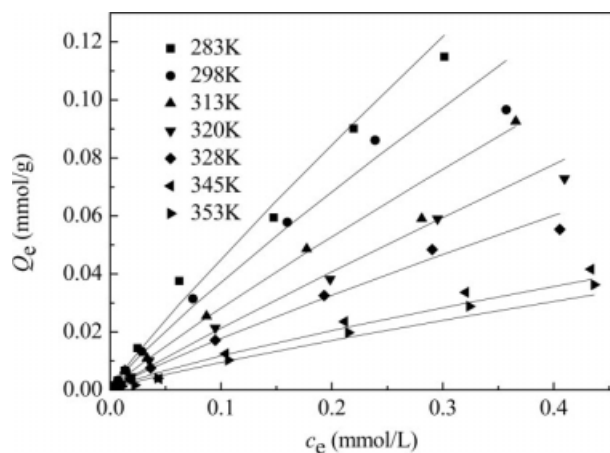


Figure 10 Adsorption equilibrium isotherm of benzidine adsorbed on CD copolymer.

Q_e . The Freundlich adsorption isotherms of benzidine adsorbed on CD copolymer are presented in Figure 11. The empirical constants K_f , $1/n$, and r obtained from Figure 11 are listed in Table II. The correlation coefficient varying from 0.9834 to 0.9993 indicates that the inclusion adsorption of benzidine on CD copolymer is consistent with the Freundlich isotherm equation. The value of K_f decreased with the increment of temperature, which indicated that the adsorptivity reduced with the enhancement of temperature.

The Langmuir model represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies and no interaction between sorbed molecules.¹⁸ The linearized form of the Langmuir isotherm corresponds to the following equation:

$$\frac{c_e}{Q_e} = \frac{1}{bQ_m} + \frac{c_e}{Q_m} \quad (5)$$

where Q_m is the maximum sorption capacity, indicating a monolayer coverage of the sorbent with sorbate;

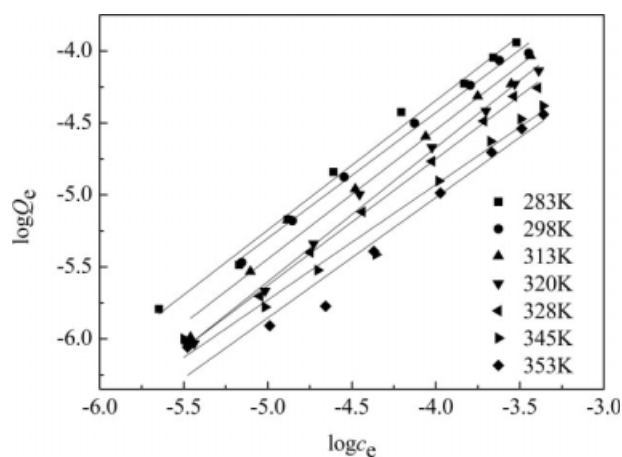


Figure 11 The Freundlich isotherms of benzidine adsorbed on the CD copolymer over the temperature range of 283–353 K.

TABLE II
Values of Different Parameters of the Freundlich Adsorption Isotherms for Benzidine at the Temperature Over the Range of 283–353 K

Temperature (K)	K_f	$1/n$	Correlation coefficient (r)
283	0.1811	0.9004	0.9961
298	0.1165	0.8735	0.9976
313	0.1110	0.8981	0.9920
320	0.1144	0.9323	0.9978
328	0.05797	0.8782	0.9993
345	0.01881	0.8007	0.9879
353	0.02124	0.8363	0.9834

and b is related to the energy or net enthalpy of the adsorption, and is independent from temperature.

Take the adsorption equilibrium at 313 K, for example. When fitting the data to the Langmuir equation, the correlation coefficient is 0.5427, which means the Langmuir model cannot represent the inclusion adsorption procedure. We can conclude that the inclusion adsorption of CD copolymer is different from monolayer adsorption. The linearization form of the Langmuir isotherm is shown in Figure 12.

The value of the equilibrium constant K_c was determined with the following equation:

$$K_c = \frac{F_e}{1 - F_e} \quad (6)$$

where F_e is the fraction of benzidine adsorbed on CD copolymer at equilibrium.

The thermodynamic parameters of enthalpy (ΔH^\ominus), entropy (ΔS^\ominus), and Gibbs free energy (ΔG^\ominus) were estimated as:

$$\Delta G^\ominus = -RT \ln K_c \quad (7)$$

$$\ln K_c = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R} \quad (8)$$

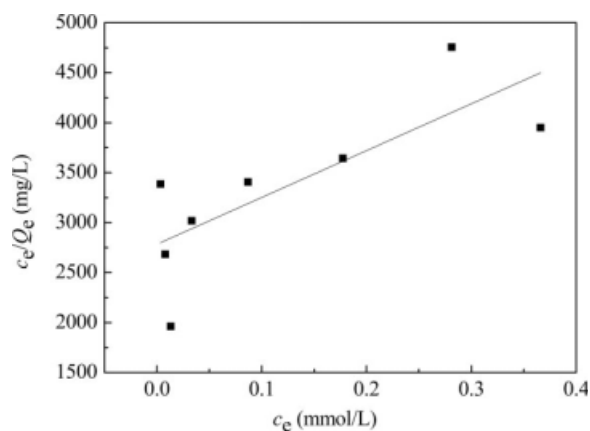


Figure 12 The Langmuir isotherm of benzidine adsorbed on the CD copolymer at 313 K.

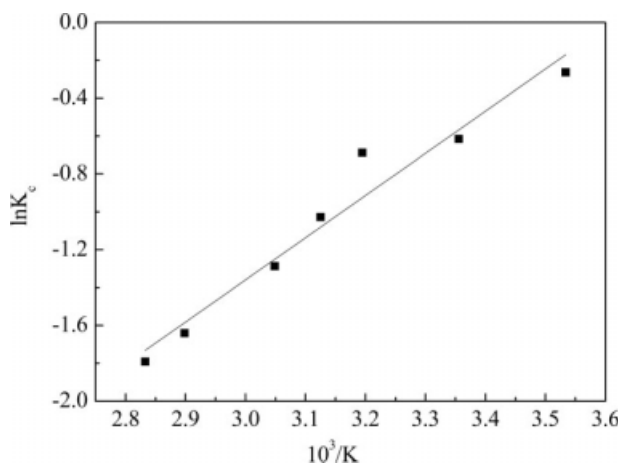


Figure 13 Variation of sorption equilibrium of benzidine on CD copolymer with temperature.

The linear relationship of $\ln K_c$ versus $1/T$ using 0.050 g of CD copolymer and 25 mL of 100 $\mu\text{g/mL}$ initial benzidine concentration at $\text{pH} = 7$ was shown in Figure 13. The ΔH^\ominus and ΔS^\ominus of the inclusion adsorption could be calculated from the slopes and intercepts of the plots.

The linear correlation coefficient of $\ln K_c$ versus $1/T$ is 0.9748, and the results of ΔH^\ominus , ΔS^\ominus , and ΔG^\ominus of benzidine inclusion adsorption¹⁵ on CD copolymer were -18.5272 kJ/mol, -66.8854 J/(mol K), and -257.4530 J/mol, respectively. The negative values of ΔH^\ominus and ΔS^\ominus show that the inclusion adsorption of benzidine on CD copolymer is exothermic. The value of ΔG^\ominus indicates that the sorption process is spontaneous in nature.

CONCLUSION

β -CD was crosslinked by HMDI, and its inclusion adsorption behavior was investigated. The obtained CD copolymer contained a range of 0.3957–0.4058 mmol/g CD, which was detected by elemental analysis. The physical and chemical properties of CD copolymer were characterized by SEM, FTIR, DSC, TGA, XRD, and BET N_2 adsorption. The inclusion adsorption of benzidine by CD copolymer was observed at a relatively low initial concentration level, indicating its high applicability to remove these organics from water. Comparing CD copolymer with activated carbon, lower equilibrium concentration and less equilibrium time were observed. The thermodynamic constants ΔH^\ominus , ΔS^\ominus , and ΔG^\ominus of the inclusion adsorption demonstrate that the adsorption of organics on CD copolymer is exothermic. The Freundlich equation could be employed to describe the procedure of the adsorption of benzidine on CD copolymer.

References

1. Engeldinger, E.; Armspach, D.; Matt, D. *Chem Rev* 2003, 103, 4147.
2. Hapiot, F.; Tilloy, S.; Monflier, E. *Chem Rev* 2006, 106, 767.
3. Rekharsky, M. V.; Inoue, Y. *Chem Rev* 1998, 98, 1875.
4. Ma, M.; Li, D. *Chem Mater* 1999, 11, 872.
5. Ju, J. F.; Syu, M. J.; Teng, H. S.; Chou, S. K.; Chang, Y. S. *Sens Actuators B* 2008, 132, 319.
6. Hsieh, R. Y.; Tsai, H. A.; Syu, M. J. *Biomaterials* 2006, 27, 2083.
7. Breslow, R.; Dong, S. D. *Chem Rev* 1998, 98, 1997.
8. Cavalli, R.; Trotta, F.; Tumiatti, W. *J Incl Phenom Macrocyclic Chem* 2006, 56, 209.
9. Yu, J. C.; Jiang, Z. T.; Liu, H. Y.; Yu, J.; Zhang, L. *Anal Chim Acta* 2003, 477, 93.
10. Li, D.; Ma, M. *Sens Actuators B* 2000, 69, 75.
11. Thuaut, P. L.; Martel, B.; Crini, G.; Maschke, U.; Coqueret, X.; Morcellet, M. *J Appl Polym Sci* 2000, 77, 2118.
12. Lee, K. P.; Choi, S. H.; Ryu, E. N.; Ryoo, J. J.; Park, J. H.; Kim, Y.; Hyun, M. H. *Anal Sci* 2002, 18, 31.
13. Asthana, A.; Bose, D.; Durgbanshi, A.; Sanghi, S. K.; Kok, W. T. *J Chromatogr A* 2000, 895, 197.
14. Saenger, W.; Jacob, J.; Gessler, K.; Steiner, T.; Hoffmann, D.; Sanbe, H.; Koizumi, K.; Smith, S. M.; Takaha, T. *Chem Rev* 1998, 98, 1787.
15. Bhaskar, M.; Aruna, P.; Jeevan, R. J. G.; Radhakrishnan, G. *Anal Chim Acta* 2004, 509, 39.
16. Wei, F. S. *Analytical Technique of Water and Waste Water*; China Environmental Science Press: Beijing, 2002.
17. Akhtar, M.; Bhangar, M. I.; Iqbal, S.; Hasany, S. M. *J Agric Food Chem* 2005, 53, 8655.
18. Martel, B.; Thuaut, P. L.; Bertini, S.; Crini, G. G.; Bacquet, M.; Torri, G.; Morcellet, M. *J Appl Polym Sci* 2002, 85, 1771.