Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 72 (2008) 456–461
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Preparation and adsorption property of chitosan beads bearing β-cyclodextrin cross-linked by 1,6-hexamethylene diisocyanate

Fei Zha *, Shaoguang Li, Yue Chang

College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

Received 28 March 2007; received in revised form 16 July 2007; accepted 12 September 2007
Available online 20 September 2007

Abstract

Glutaraldehyde activated chitosan beads bearing β-cyclodextrin cross-linked by 1,6-hexamethylene diisocyanate was prepared, and characterized by IR, XRD and TG-DTA. Its adsorption property of hydroquinone was investigated by spectrophotometry. The adsorption capacity increases with increasing temperature and pH value. The adsorption process can be better simulated by Freundlich isotherm equation ($R^2 > 0.996$) and the thermodynamic parameters such as free energy change, enthalpy change and entropy change were calculated. The adsorption of hydroquinone on chitosan beads bearing β-cyclodextrin cross-linked by 1,6-hexamethylene diisocyanate is a spontaneous, endothermic and random process.

Keywords: Chitosan beads; β-Cyclodextrin; 1,6-Hexamethylene diisocyanate; Hydroquinone; Adsorption; Thermodynamics

1. Introduction

Hydroquinone and other phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides, insecticides etc. Degradation of these substances results in the appearance of phenol and its derivatives in the environment. Most of these compounds are recognized as toxic carcinogens. The presence even in low concentration causes unpleasant taste and odor of drinking water and can exert negative effects on different biological processes. Different methods designed to remove phenols have been proposed. Adsorption is the best and most frequently used method. Thus, many adsorbents, such as activated carbon (Gupta, Ali, & Saini, 2004; Kumar, Kumar, & Kumar, 2003; Mohamed, Khater, & Mostafa, 2006; Mohan, Gupta, Srivastava, & Chander, 2000; Roostaei & Tezel, 2004), modified bentonites (Yıldız, Gönülşen, Koyuncu, & Çalıml, 2005) have been designed. Recently, the usage of natural and chlorinated adsorbents for wastewater treatment is increasing because of their abundance, low price and lack of toxicity (Gupta, Saini, & Jain, 2005; Gupta, Shrivastava, & Jain, 2001).

Chitosan is a biodegradable and a nontoxic copolymer of glucosamine and *N*-acetylglucosamine derived from the natural polymer chitin, which is commercially available. Chitosan has a highly reactive amino group is a useful material for various purposes such as ion-exchange (Muzzarelli & Rocchetti, 1974) and functional matrixes (Xia, Guo, Song, Zhang, & Zhang, 2006). Recently, immobilization of cyclodextrins in cross-linked chitosan has received considerable attention, because their physical properties, inclusion and adsorption behaviors are different from those of natural cyclodextrins and chitosan (Cerchiara, Luppi, Bigucci, & Zecchi, 2003; Chiu, Chung, Giridhar, & Wu, 2004; Tojima et al., 1999). The chitosan bearing β-cyclodextrin materials were used for adsorption of *p*-nonylphenol, bisphenol A and other phenolic compounds (Aoki, Nishikawa, & Hattori, 2003). However, little data are available on the adsorption of phenolic compounds by these materials.

In this paper, glutaraldehyde activated chitosan beads bearing β-cyclodextrin cross-linked by 1,6-hexamethylene diisocyanate was synthesized and characterized. The ther-

* Corresponding author. Tel.: +86 0931 7972015; fax: +86 0931 7972989.
E-mail address: feizha70@sina.com (F. Zha).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.09.013

modynamic parameters of the adsorption of hydroquinone on synthesized chitosan beads were investigated, and the adsorption thermodynamic parameters were calculated.

2. Experimental

2.1. Materials and instruments

The purification of chitosan (degree of deacetylation is 91%, mensurated by alkali titration) was attained through the method of to Matteus, F.A.G. (Matteus, 1997). β-Cyclodextrin (β-CD) was treated with absolute ethanol, following washed with double distilled water for three times, dried and kept in a desiccator before used. 1,6-Hexamethylene diisocyanate (HMDI), glutaraldehyde (50%, v/v), hydroquinone, DMF, and all other chemicals used were analytical grade.

The products were characterized by comparison of their spectral characteristics and physical data with authentic samples. FT-IR spectra were taken with KBr pellets on an Equinox55 FT-IR spectrophotometer (Brucker, Germany). X-ray diffraction (XRD) studies were performed by using D/max-2400 X-ray diffractometer (Rigaku, Japan) with CuKa as radiation source. TG-DTA was determined with a SSC-5200 thermogravimetric analyzer (Perkin-Elmer, American) under nitrogen atmosphere. The adsorption experimental was carried out at constant temperature controlled by a SHA-B Shaker (Jiangsu, China) with a precision of ±0.5 K. The absorption spectra were recorded by Agilent UV-8453A spectrophotometer at $\lambda_{max} = 289$ nm.

2.2. Preparation of chitosan beads bearing β-cyclodextrin

Glutaraldehyde was cross-linked to chitosan macromolecule by an inverse emulsion polymerization method to form microspheres as follows: 75 ml of 2.5% (w/w) chitosan solution was dissolved in 2% (w/v) aqueous acetic acid solution. After the powder was completely dissolved, it was poured into the dispersion medium, which was composed of 150 ml of paraffin oil and 1.5 ml of Span 80. During these processes, the dispersion medium was vigorously stirred with a magnetic stirrer at 650 rpm at room temperature. After stirring for about 30 min, 15 ml of 50% glutaraldehyde solution was added dropwise into the dispersion medium and then stirred for 0.5 h at 323 K. At the end of this period, the NaOH aqueous solution was dropped into the mixture to adjust the pH to 7.0. Then the emulsion was kept on stirring at constant temperature for 1.5 h. Finally, the beads were collected by filtration and extracted with petroleum ether in the sorbitic extractor for 24 h, then washed with ethanol, redistilled water consecutively, dried and kept in a desiccator before use.

Prepared chitosan beads (4.0 g) were added to 100 ml of a mixture containing of 5% (v/v) HMDI of toluene solution. After stirring for 1 h at 323 K, the supernatant was discarded and 100 ml of DMF solution containing 2% (w/v) β-CD was added. The mixture was magnetically stirred for 1 h. The supernatant was decanted and the β-CD immobilized chitosan beads (CS-β-CD) were washed several times with redistilled water followed by ethanol and finally with redistilled water before dried. The contents of the β-CD moiety in CS-β-CD were determined by the phenol–sulfuric acid method. Degree of substitution by the β-cyclodextrin of the above product was 4.3%.

The synthesis is summarised in Scheme 1.

2.3. Adsorption experiments

In each adsorption experiment, 20 ml of hydroquinone solution of known concentration (from 11.011 to 110.11 mg/l) was added to a 50 ml Erlenmeyer flask containing of 50 mg of CS-β-CD. It was shaken at 180 rpm continuously at the constant temperature. At a predetermined time, the suspension was subjected for centrifugation and the final hydroquinone concentration of the supernatant was determined spectrophotometrically.

2.4. Mathematical procedures

The quantity of hydroquinone adsorbed on CS-β-CD were quantified by mass balance. The following parameters were used.

Adsorption capacity of the adsorbent (q_e) expressed in terms of the hydroquinone amount adsorbed on the unit adsorbent mass (mg/g):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of the hydroquinone solution (mg/l), respectively, and m is the dosage of CS-β-CD (g).

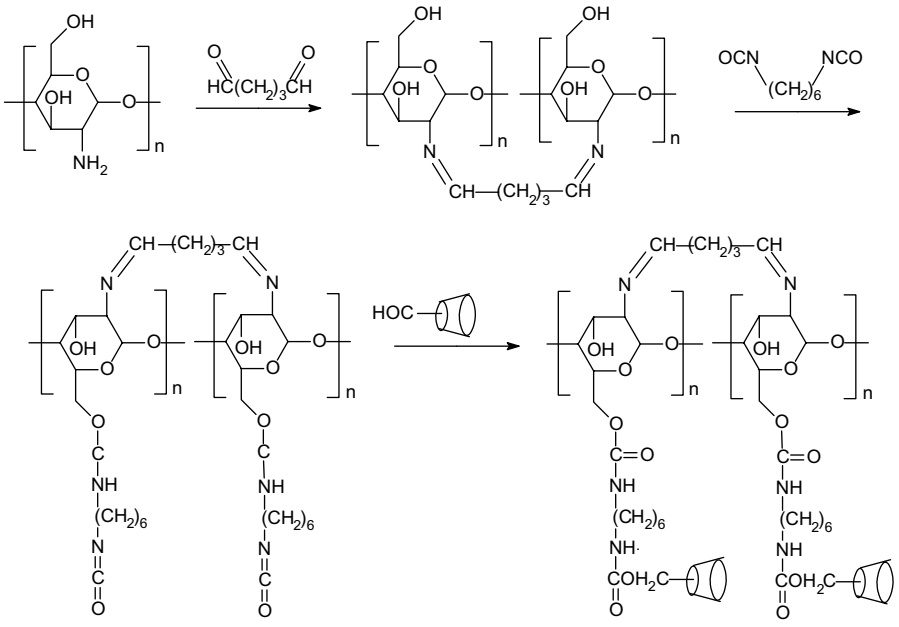
In order to optimize the design of a sorption system to remove hydroquinone from effluents, it is important to establish an appropriate correlation for the equilibrium curve. The Langmuir isotherm Eq. (2) and the Freundlich isotherm Eq. (3) were used to model the adsorption equilibrium data.

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QkC_e} \tag{2}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

In the above equations, Q is the maximum amount of the hydroquinone per unit weight of CS-β-CD (mg/g). k is the Langmuir constant related to the affinity of the binding sites. K_f and $1/n$ are Freundlich constants related to the adsorption capacity and the adsorption efficiency, respectively.

The Langmuir constant k is related to the enthalpy of adsorption (Gupta, Ali, Suhas, & Mohan, 2003). Therefore, the thermodynamic parameters including the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were also evaluated using the following equations (Lyubchik et al., 2004; Rattanaphani, Chairat, Bremner, & Rattanaphani, 2007):



Scheme 1. Preparation of β-CD-linked chitosan beads.

$$\Delta G = -RT\ln(k) \tag{4}$$

$$\ln(b) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR spectra

Fig. 1 shows the IR spectra of chitosan (CS), chitosan beads and CS-β-CD.

When chitosan is cross-linked by glutaraldehyde, it can be seen that the two peaks of chitosan beads at 2929 cm^{-1} and 2870 cm^{-1} are stronger than that of chitosan, especially at 2929 cm^{-1}. This indicates that a number of methyl groups are substituted on to the natural polymer. The peak shows at 1599 cm^{-1} disappeared and a characteristic absorption band observed near 1640 cm^{-1} attributed to the C═N vibrations of Schiff base imines. When β-CD is immobilized on chitosan beads using HMDI as a cross-linker, the peak at 2929 cm^{-1} is much stronger, which shows that more methyl groups are formed within the beads. The absorption band at 1250 cm^{-1} could be attributed to the C═O characteristic vibrations of aliphatic polyurethane. The 850 cm^{-1} peak is the characteristic bands of α-(1,4) glucopyranose in β-CD. On the other hand, there is no evidence of characteristic bands of the free isocyanate groups near 1665 cm^{-1}.

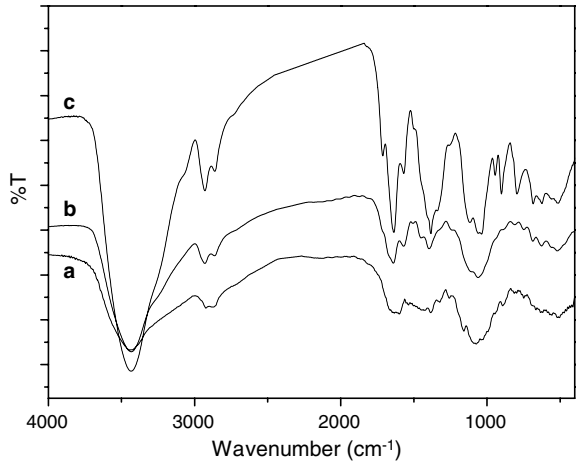


Fig. 1. IR spectra of chitosan (a), chitosan beads (b) and CS-β-CD (c).

3.1.2. XRD spectra

Further evidence of formation was obtained by X-ray power diffraction (XRD) as demonstrated in Fig. 2. The diffraction pattern of pure chitosan presents three peaks at $2\theta = 10°$, 20° and 27°, respectively. When chitosan are cross-linked by glutaraldehyde, the peak at $2\theta = 20°$ is weaker than that of chitosan, and the peak at $2\theta = 27°$ is not observed. This due to the O of the carbonyl groups of glutaraldehyde being supplanted by the N in the amino groups of chitosan to form a Schiff base, which could weaken the hydrogen bond of chitosan. When β-CD is immobilized to chitosan beads using HMDI as a cross-linker, the peak at $2\theta = 20°$ is weaker, which indicates that the degree of crystallinity, of the resulted resin decreases more. The peak around $2\theta = 22.5°$ is the characteristic bands of β-CD.

3.1.3. TG/DTA

TG cures of chitosan, chitosan beads and CS-β-CD are shown in Fig. 3. Chitosan degrades in two stages. The first

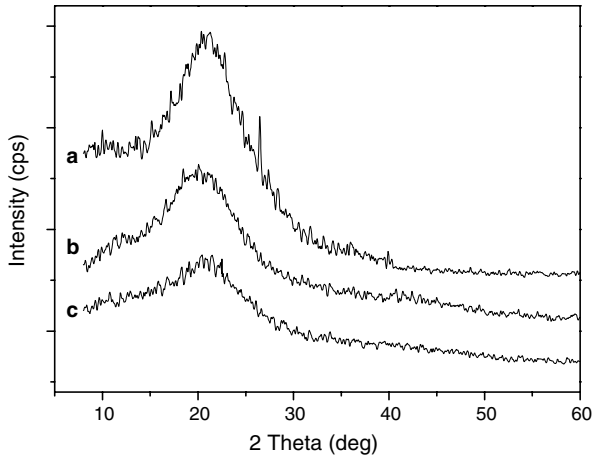


Fig. 2. Powder XRD of chitosan (a), chitosan beads (b) and CS-β-CD (c).

stage stares at about 330.9 K with weight loss of about 5%. The second stage starts at about 583 K and reaches a maximum at with weight loss of 60%. The chitosan beads show two degradation stages. The first stage starts at about 337.6 K with a weight loss of 6.5% due to the loss of water. The second degradation stage of chitosan beads at about 510 K and reaches a maximum at 673 K with weight loss of 50%. The first degradation stage of CS-β-CD starts at about 341.7 K with weight loss of 1.77%. The second degradation stage of CS-β-CD starts at about 514 K and reaches a maximum at 673 K with weight loss of 44%. The second degradation stage of chitosan takes place at higher temperatures than that of the chitosan beads and CS-β-CD, which can be seen from the DTG cure (dashed lines) more accurately. This indicates that all the modified chitosan is less stable than the chitosan due to the weakening of the hydrogen bonding as a result of the cross-linking.

Differential thermal analysis (DTA) cures of corresponding compounds are shown in Fig. 4. Two exothermic peaks observed are corresponded to the loss of water and the heat decomposition of chitosan. The lower decomposition temperature of modified chitosan derivatives corresponds to the decomposition of less organized chitosan molecules. Although the peak area at the decomposition temperature of chitosan is larger than that of the CS beads and CS-β-CD, it decomposes at a higher temperature.

3.2. Adsorption of hydroquinone experiments

3.2.1. Effect of contact time on the adsorption

Before the adsorption thermodynamic studies, it is necessary to determine the equilibrium contact time. Twenty portions of hydroquinone solutions (20 ml, 55.055 mg/l) were prepared. Each was contacted with 0.05 g of chitosan-β-CD at a fixed neutral pH and shake at a constant temperature of 293 K. At scheduled time, one of the mixtures was taken from the shaker and the concentration was measured by spectrophotometry. By plotting the adsorption capacity of the adsorbent against the time, it was found that the adsorption system could be reached equilibrium after 10 h (see Fig. 5). Therefore, all thermodynamic measures were performed under these condition.

3.2.2. Effect of acidity on the adsorption

Influence of acidity on the adsorption was studied at the pH ranged from 2.0 to 11.0. Result shows the adsorption of hydroquinone by CS-β-CD increases with the increase of pH (see Fig. 6).

3.2.3. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. The adsorption of hydroquinone at different temperatures was measured and the adsorption isotherms are shown in Fig. 7.

When $1/q_e$ was plotted against $1/C_e$ according to Eq. (2), the Langmuir model fitted the experimental data very well with high correlation coefficients ($R^2 > 0.98$). The values of the Langmuir constants Q and k at different temperatures were calculated from the intercepts and slopes of different straight lines, respectively. The calculated results

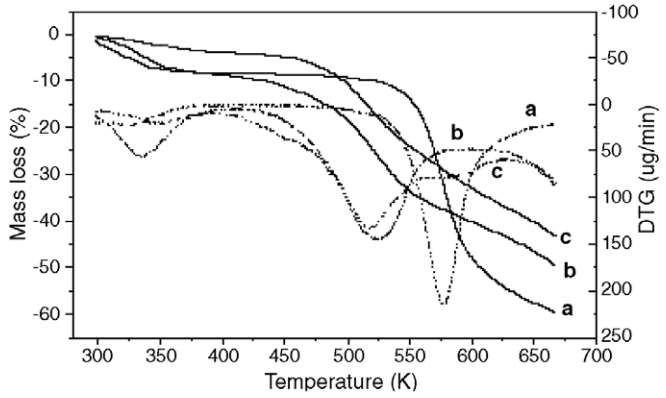


Fig. 3. TGA/DTG cure of chitosan (a), chitosan beads (b) and CS-β-CD (c).

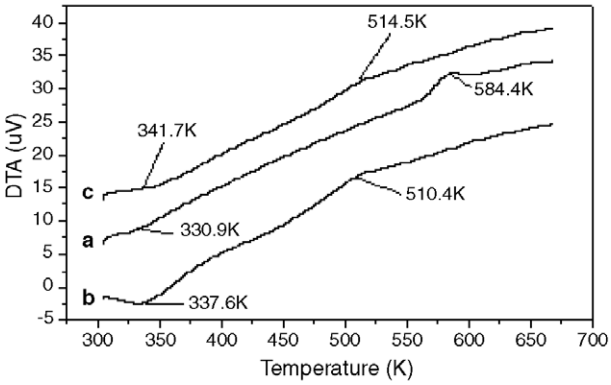


Fig. 4. TDA cure of chitosan (a), chitosan beads (b) and CS-β-CD (c).

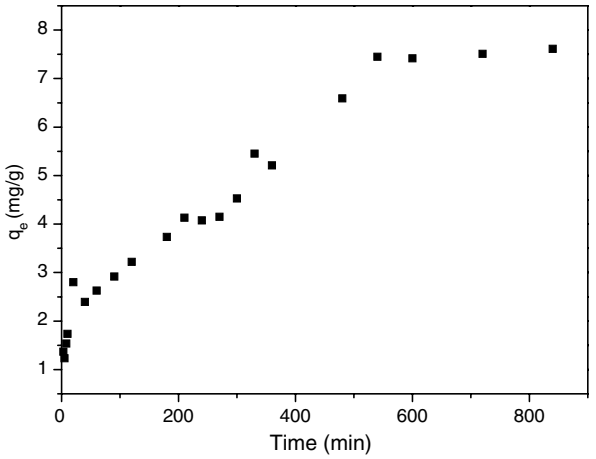


Fig. 5. Equilibrium contact time for hydroquinone.

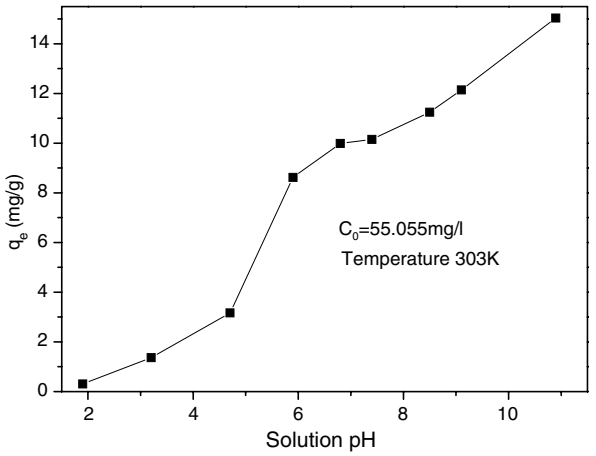


Fig. 6. Effect of pH on the adsorption of hydroquinone.

are reported in Table 1. The increase in the values of Q shows that the adsorption rate increases with increasing temperature.

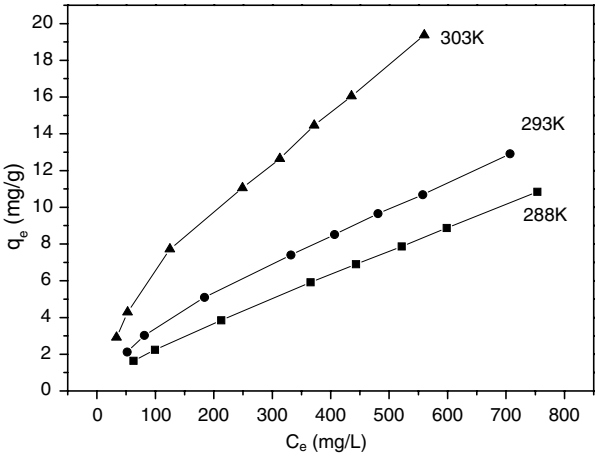


Fig. 7. Adsorption isotherms for the adsorption of hydroquinone at three temperatures.

Table 1
Langmuir and Freundlich isotherm constants for the adsorption of hydroquinone on chitosan-β-CD at different temperatures

Temp (K)	Langmuir			Freundlich		
	Q (mg/g)	k (ml/mg)	R^2	K_f (mg/g)	$1/n$	R^2
288	15.31	16.76	0.9898	0.3684	0.75693	0.9988
293	16.11	26.21	0.9947	0.6707	0.67296	0.9990
303	23.31	38.55	0.9972	1.3230	0.64685	0.9964

A linear relationship was also observed when Freundlich equation was used to simulate the thermodynamic data. The higher correlation coefficients ($R^2 > 0.996$, see Table 1) means the Freundlich equation is more suitable for the adsorption. The value of K_f is related to the degree of adsorption. The increase in the values of K_f at higher temperatures shows that the adsorption rate increases with the rise of temperature. The values of $0.1 < 1/n < 1.0$ shows that adsorption of hydroquinone on the anion exchanger is favorable (McKay, Blair, & Garden, 1982).

3.2.4. Adsorption thermodynamic parameters

The free energy change (ΔG) was evaluated using Eq. (4), while enthalpy change (ΔH) and entropy change (ΔS) of the adsorption were calculated from the slope and intercept of the straight line of ln (k) versus $1/T$ according to Eq. (5). Thermodynamic parameters for the adsorption reported in Table 2 show the free energy of the process at all temperatures was negative and decreased with the rise in temperature. This indicates that the adsorption process is spontaneous. The overall process seems to be endothermic. If physical sorption were the only adsorption process, the enthalpy of the system would be exothermic (Lyubchik et al., 2004). This indicates that adsorption of hydroquinone on the CS-β-CD is rather complex, involving both chemical adsorption and the inclusion in β-CD are included. It can be ensured from the IR spectra of hydroquinone adsorbed by CS-β-CD and crossblended with CS-β-CD shown in Fig. 8. The peaks at 1463 and 1360 cm^{-1} are the characteristic bands of hydroquinone crossblended with CS-β-CD, while its moved to 1451 cm^{-1} and 1375 cm^{-1} when hydroquinone is adsorbed by CS-β-CD. The positive entropy change (ΔS) indicates that the reorientation or restructuring of water around the solute or surface is very unfavorable, since it disturbs the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. As a result of adsorption of hydroquinone onto CS-β-CD

Table 2
Thermodynamic parameters for the adsorption of hydroquinone on chitosan-β-CD at different temperatures

Temp (K)	k (ml/mg)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)	R^2
288	16.76	−6.75			
293	26.21	−7.96	38.74	158.5	0.9524
303	38.55	−9.20			

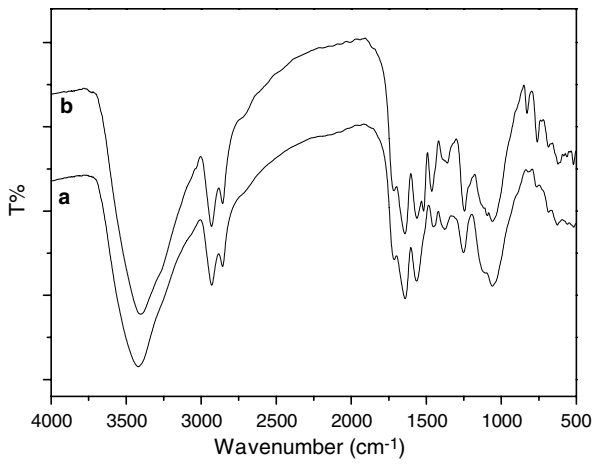


Fig. 8. IR spectra of adsorbed CS-β-CD (a) and crossblended CS-β-CD with hydroquinone (b).

surface, the liberation of the solvent molecules from the solvated shells is more predominate in the studied system and, thus, the degree of freedom of the water molecule increases. Therefore, the positive value of entropy suggests the increased randomness at the solid-solution interface during the adsorption of hydroquinone (Iqbal & Ashiq, 2007).

4. Conclusion

Chitosan beads bearing β-cyclodextrin was prepared by activated chitosan with glutaraldehyde, followed by cross-linked with 1,6-hexamethylene diisocyanate and reacted with β-cyclodextrin. It was characterized by the methods of IR, XRD and TG-DTA.

The adsorption properties of synthesized chitosan beads bearing β-cyclodextrin for hydroquinone were studied. The adsorption capacity increases with increasing temperature and pH value.

Both the Langmuir and Freundlich isotherm equations could be used to modeling the adsorption process, but the later is more suitable. The thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. The adsorption is a spontaneous, endothermic and a random process.

Acknowledgement

This work was supported by the fund of Key Laboratory of Polymer Material of Gansu Province.

References

Aoki, N., Nishikawa, M., & Hattori, K. (2003). Synthesis of chitosan derivatives bearing cyclodextrin and adsorption of *p*-nonylphenol and bisphenol A. *Carbohydrate Polymers, 52*, 219–223.

Cerchiara, T., Luppi, B., Bigucci, F., & Zecchi, V. (2003). Effects of chitosan on progesterone release from hydroxypropyl-β-cyclodextrin complexes. *International Journal of Pharmaceutics, 258*, 209–215.

Chiu, S. H., Chung, T. W., Giridhar, R., & Wu, W. T. (2004). Immobilization of β-cyclodextrin in chitosan beads for separation of cholesterol from egg yolk. *Food Research International, 37*, 217–223.

Gupta, V. K., Ali, I., & Saini, V. K. (2004). Removal of chlorophenols from wastewater using red mud: An aluminum industry waste. *Environmental Science & Technology, 38*, 4012–4018.

Gupta, V. K., Ali, I., Suhas & Mohan, D. (2003). Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *Journal of Colloid and Interface Science, 265*, 257–264.

Gupta, V. K., Saini, V. K., & Jain, N. (2005). Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science, 288*(1), 55–60.

Gupta, V. K., Shrivastava, A. K., & Jain, N. (2001). Biosorption of chromium(VI) from aqueous solutions by green algae spirogyra species. *Water Research, 35*, 4079–4085.

Iqbal, M. J., & Ashiq, M. N. (2007). Adsorption of dyes from aqueous solutions on activated charcoal. *Journal of Hazardous Materials, 139*, 57–66.

Kumar, A., Kumar, S., & Kumar, S. (2003). Adsorption of resorcinol and catechol on granular activated carbon: Equilibrium and kinetics. *Carbon, 41*, 3015–3025.

Lyubchik, S. I., Lyubchik, A. I., Galushko, O. L., Tikhonova, L. P., Fonseca, I. M., & Svetlana, B. (2004). Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 242*, 151–158.

Matteus, F. A. G. (1997). *Application of chitin and chitosan*. Switzerland: Technomic Publishing AG.

McKay, G., Blair, H. S., & Garden, J. R. (1982). Adsorption of dyes on chitin I. Equilibrium studies. *Journal of Applied Polymer Science, 27*, 3043–3057.

Mohamed, F. S., Khater, W. A., & Mostafa, M. R. (2006). Characterization and phenols sorptive properties of carbons activated by sulphuric acid. *Chemical Engineering Journal, 116*, 47–52.

Mohan, D., Gupta, V. K., Srivastava, S. K., & Chander, S. (2000). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 177*, 169–181.

Muzzarelli, R. A. A., & Rocchetti, R. (1974). The determination of vanadium is sea water by hot graphite atomic absorption spectrometry on chitosan after separation from salt. *Analytica Chimica Acta, 70*, 283–289.

Rattanaphani, S., Chairat, M., Bremner, J. B., & Rattanaphani, V. (2007). An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan. *Dyes and Pigments, 72*, 88–96.

Roostaei, N., & Tezel, F. H. (2004). Removal of phenol from aqueous solutions by adsorption. *Journal of Environment Management, 70*, 157–164.

Tojima, T., Katsura, H., Nishiki, M., Nishi, N., Tokura, S., & Saksiri, N. (1999). Chitosan beads with pendant α-cyclodextrin: Preparation and inclusion property to nitrophenolates. *Carbohydrate Polymers, 40*, 17–22.

Xia, Y. Q., Guo, T. Y., Song, M. D., Zhang, B. H., & Zhang, B. L. (2006). Selective separation of quercetin by molecular imprinting using chitosan beads as functional matrix. *Reactive and Functional Polymers, 66*, 1734–1740.

Yıldız, N., Gönülşen, R., Koyuncu, H., & Çalıml, A. (2005). Adsorption of benzoic acid and hydroquinone by organically modified bentonites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 260*(1–3), 87–94.