Preparation and Sorption Studies of β-Cyclodextrin/Epichlorohydrin Copolymers

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ABSTRACT: β-Cyclodextrin (β-CD) copolymer materials were synthesized by reacting different mole ratios (1 : 15, 1 : 25 and 1 : 35) of β-CD with epichlorohydrin (EP). The products were characterized using N_2 porosimetry, Fourier Transform Infrared spectroscopy, ^{13}C CP-MAS NMR spectroscopy, thermogravimetry analysis, elemental (C and H) analysis, and scanning electron microscopy. The sorption properties in aqueous solution were studied using p-nitrophenol (PNP) with UV–Vis spectrophotometry. Sorption isotherms were obtained at pH 4.6 and three temperatures (22, 35, and 45°C) and at pH 10.3 at 22°C. The isotherms were analyzed using the BET isotherm model and the sorption parameters provided estimates of the surface area, sorption capacity, and isosteric heats of sorption for each polymeric material. The estimated surface areas are as follows: 58.2, 52.1, and 90.1 m^2/g at pH 4.6. At pH 10.3, the estimated surface areas are 44.2, 40.5, and 58.5 m^2/g, respectively. The removal efficiency of PNP by the polymeric materials ranged between 4.5 and 58% for the conditions investigated whereas the isosteric heats ranged between −24.5 and −13.6 kJ/mol. Removal efficiencies were concluded to strongly depend on the sorption conditions such as pH, temperature, and the relative amounts of sorbent and dye in aqueous solution. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2982–2989, 2010

Key words: adsorption; biomaterials; crosslinking; dyes/pigments; inclusion chemistry

INTRODUCTION

The occurrence and accumulation of toxic inorganic and organic pollutants in aquatic environments is well documented, as shown in the 2008 National Pollutant Release Inventory[1] and a recent report by the Polaris Institute.[2] The United Nations Environment Program (UNEP)[3] has recognized the importance of safe clean drinking water as one of the eight millennium goals. The buildup of organic pollutants in aquatic environments poses serious concerns for water quality and human health issues. Agrochemicals, such as dinitrophenol derivatives, pose serious environmental and human health concerns owing to their toxicity, carcinogenic properties, and their widespread agricultural application.[4,5] Ultrafiltration processes represent a green strategy for remediation of contaminated waters;[6] however, there is a need to develop novel engineered materials with improved physicochemical properties for targeted sequestration of inorganic and organic pollutants.

Cyclodextrins (CDs) have a unique toroidal molecular shape and their inclusion chemistry has been the subject of many studies.[7] β-cyclodextrin (β-CD) is among the most commonly studied[8,9] (Fig. 1) and copolymer materials that incorporate β-CD into the polymeric framework (cf. Scheme 1) are of great interest in sorption-based applications.[10,11] The sorption of adsorbates in β-CD copolymer materials may occur at various sorption sites (e.g., intracavity vs. extracavity sites), such as the β-CD cavity or interstitial domains of the polymer framework.[12–21]

Water insoluble β-CD/epichlorohydrin (EP) based copolymers are typically designed by controlling the molar ratios of monomers, base concentration, temperature, stirring rate, and reaction time.[5,22] Synthetically engineered polymer materials[22] of this type provide a route to variable crosslink density, variable surface area, pore structure properties, and tunable sorption characteristics. Changes in the relative mole ratio of β-CD (monomer A) to EP (monomer B) may alter the repeat structure of the monomer units from an A-B to an $A-B_n$ type copolymer; the latter type contains EP rich domains that are hydrophilic in nature with sorption characteristics and physiochemical properties that are unique compared with typical A-B type copolymers. In this research, we report the preparation and characterization of
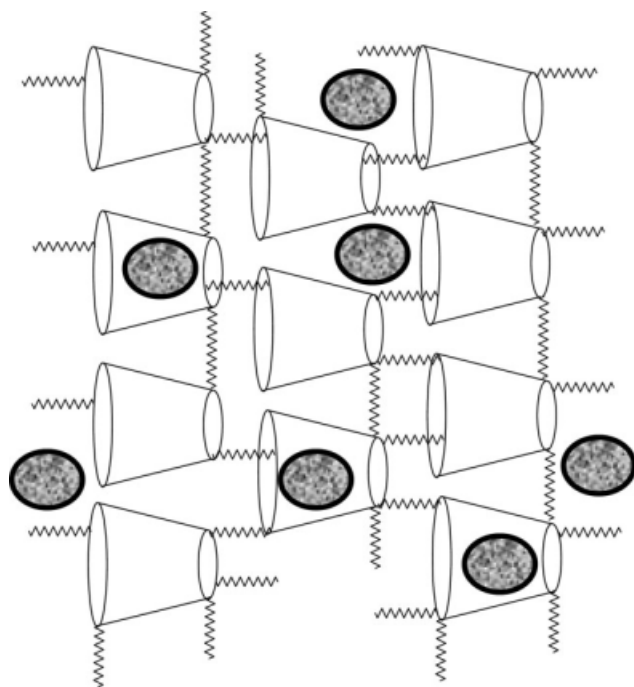
Scheme 1 The extended framework structure of a cross linked β-CD/EP polymer containing an adsorbed guest molecule (sphere) within the β-CD inclusion sites (tori interior) and the interstitial sites (tori exterior) of the polymeric framework. The line segments connecting the β-CD tori represent the cross linker (i.e. epichlorohydrin) molecule.

several β-CD/EP polymeric materials and their equilibrium sorption properties with p-nitrophenol (PNP) in aqueous solution. Using this dye-based method, the sorption isotherms for polymers with PNP were obtained using UV–Vis spectrophotometry at pH 4.6 and 10.3, and at various temperatures (22, 35, and 45°C). Variations of the β-CD/EP copolymer composition were studied to examine the effects of surface area and pore structure properties on the sorption capacity and thermodynamics of sorption for such engineered polymeric materials. The results of this study are significant because the systematic variation of the copolymer composition and experimental conditions provides a more detailed understanding of the copolymer sorption mechanism with p-nitrophenol in aqueous solutions.

EXPERIMENTAL

Materials

β-CD and EP were both Aldrich products and used as received without further purification. The synthesis of β-CD/EP based copolymers was adapted from a published procedure.[22] The adapted protocol for the β-CD/EP polymeric materials (1 : 25 and 1 : 35) was similar except that the EP was added dropwise (~ 0.05 mL min^{-1}) in contrast to complete and rapid

addition of EP for the 1 : 15 copolymer material. The products were precipitated with ACS grade acetone and filtered after several washings of cold acetone and Millipore water to remove any starting materials. The products were crushed before drying in a pistol dryer under vacuum with P_2O_5 at 50°C overnight followed by grinding in a mortar and pestle and passed through a 40 mesh sieve.

Materials characterization

The copolymers were characterized using TGA, ^{13}C NMR using cross polarization with magic angle spinning (CP-MAS), elemental analysis, FTIR spectroscopy, and SEM, as previously described.[23,24] The pore structure properties, surface area, and sorption properties were evaluated using a dye-based UV–Vis method[23] and N_2 porosimetry.[24]

Sorption studies

PNP (Aldrich) was used as the adsorbate dye in this sorption study. Fixed amounts (~ 20 mg) of the powdered and sieved copolymer were mixed with 7 mL of dye at variable concentration (0.2–10 mM) in 10 mM potassium phosphate monobasic buffer solution and equilibrated on a horizontal shaker table for 24 h. The buffers were prepared at pH 4.6 and 10.3, respectively, to study the sorption properties of PNP in its protinated form and ionized states. The initial concentration of PNP (C_o) was determined before and after sorption (C_e) with polymers at various temperatures (22, 35, and 45°C). The estimated molar absorptivity (ε) values for PNP are $\varepsilon = 9286.5$ L mol^{-1} cm^{-1} (pH = 4.6; λ_{max}= 317 nm) and $\varepsilon = 18,478$ L mol^{-1} cm^{-1} (pH = 10.3; $\lambda_{max} = 400$ nm), respectively.[24,25] The sorption isotherms are plots of equilibrium concentration of PNP adsorbed from solution per mass of adsorbate (Q_e) versus the equilibrium concentration of unbound PNP in aqueous solution (C_e). The Q_e value is defined below where C_o is the initial PNP concentration, V is the volume of solution, and m is the mass of sorbent, as outlined previously.[22,23]

$$Q_e = \frac{(C_o - C_e) \times V}{m} \qquad (1)$$

The BET model provides an estimate of the monolayer coverage (Q_m) of the sorbent material, where PNP is the adsorbate. The dye-based sorption method[26,27] provides an independent estimate of the sorbent surface area (SA; m^2/g), as follows.

$$SA = \frac{A_m Q_m L}{N} \qquad (2)$$

where A_m represents the cross-sectional area occupied by PNP (A_m for a planar orientation is $\times 10^{-19}$
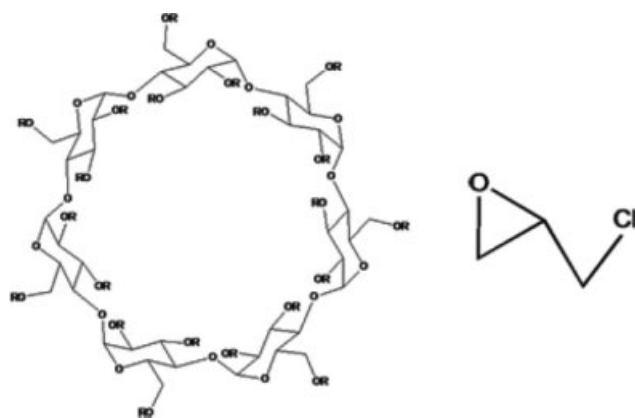
Figure 1 The molecular structures of β-cyclodextrin (where $R = H$) and epichlorohydrin.

5.25×10^{-19} m²/mol whereas an "end-on" orientation is 2.5×10^{-19} m²/mol), L is Avogadro's number (mol⁻¹), and N is the coverage factor and equals unity.[24,25]

The dye-based sorption results were well described by the BET isotherm model[26]

$$Q_e = \frac{Q_m K_{\text{BET}} C_e}{(C_s - C_e)[(1 + (K_{\text{BET}} - 1)C_e)]/C_s} \quad (3)$$

where K_{BET} is an adsorption constant, C_s is the saturated solution concentration of PNP, and Q_m is defined as in eq. (2). The best fit of eq. (3) was obtained using a nonlinear least squares fitting routine by minimizing the sum of square of errors (SSE) between the experimental and calculated sorption data. The fractional surface coverage (θ) was estimated using the value of Q_m obtained from eq. (3) and experimental Q_e estimates of selected θ values, as follows
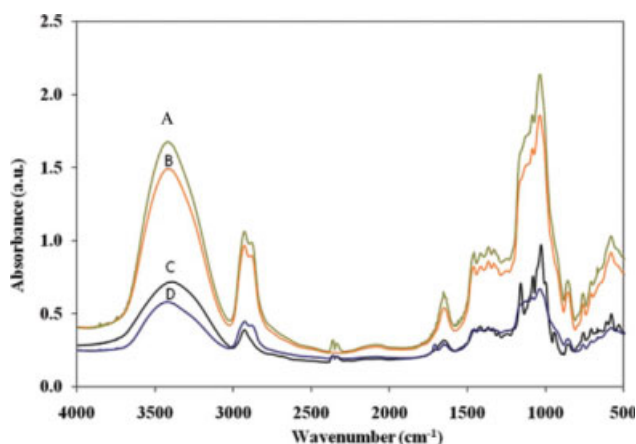

Figure 2 FTIR spectra of β-CD hydrate and cross linked β-CD with epichlorohydrin (EP) at various feed ratios where A: 1 : 35, B: 1 : 25, C: native β-CD, and D: 1 : 15 at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

TABLE I
Elemental (C and H) Analysis Results for the β-CD/ Epichlorohydrin Copolymers

Material	%C (experiment)	%C (calculated)	%H (experiment)	%H (calculated)
1 : 15	38.1	41.4	5.38	5.79
1 : 25	39.5	40.8	5.76	5.70
1 : 35	41.6	40.4	6.18	5.65
β–CD	43.4	44.5	6.59	6.22

C and H elemental analyses are uncorrected according to the estimated water content of samples.

$$\theta = \frac{Q_e}{Q_m} \quad (4)$$

RESULTS AND DISCUSSION

The copolymer materials were synthesized as water insoluble products at various β-CD/EP mole ratios (1 : 15, 1 : 25 and 1 : 35), in contrast to low molecular weight materials that are observed to be water soluble.[5,28,29] The rapid vs. dropwise addition of EP to a rapidly stirring reaction mixture provided water insoluble materials. The dropwise addition of EP is anticipated to favor the "A-B type" heteropolymer versus the "A-B$_n$ type" (where $n > 1$) materials. Depending on the formation of "A-B type" polymers *vs.* "A-B$_n$ type" copolymers, the relative amount of EP may affect the size of the pores and the accessibility of the sorption sites on the copolymer framework.

The FTIR spectra (cf. Figure 2) are shown for β-CD and the 1 : 15, 1 : 25 and 1 : 35 polymeric materials. The O—H stretching region ~ 3400 cm⁻¹, C—H stretching region ~ 2900 cm⁻¹ and C—C stretching region ~ 1600 cm⁻¹ are similar amongst the copolymers. The IR spectra are in good agreement with previous reports for such epichlorohydrin polymers.[12,17] Each of the β-CD/EP copolymers had similar IR signatures in the 3400 cm⁻¹ region (O—H stretch), 3000 cm⁻¹ (C—H stretch) and 1040 cm⁻¹ (C—O—C stretch) and these results support the product characterization. The EP linker has comparable IR vibrational bands as observed for β-CD in the following spectral regions: 3000 cm⁻¹, 1450 cm⁻¹, 1300 cm⁻¹, and 1100cm⁻¹. The relative similarity between the IR spectra for β-CD and the copolymer materials suggest that the basic structural units are preserved, in good agreement with other reports.[12,17,30]

The calculated polymer composition (C and H) are based on theoretical molecular formulae according to the synthetic feed ratios (minus HCl for each mole of EP). The TGA results for 1 : 15, 1 : 25, and 1 : 35 polymers contained 5.04, 3.60, and 4.93% water, respectively. Despite the reasonable agreement

TABLE II
Dye-Based Method Estimates of the Surface Area for
Polymeric Materials Obtained for the Sorption of PNP at
295 K and Various pH Conditions

Mole ratio (β-CD/EP)	Surface area^a (m^2/g) [pH = 4.6]	Surface area^a (m^2/g) [pH = 10.3]	Yield^b (percentage)	Surface area^c BET (m^2/g)
1 : 15	58.2	44.2	94.6	4.7
1 : 25	52.1	40.5	64.5	4.70 (0.2)^d
1 : 35	90.1	58.5	31.9	3.67

^{a} Dye-based method surface area estimates obtained from eq. (2) using a value for A_m for the planar orientation of PNP and a Q_m value estimated from eq. (6).
^{b} Yields are calculated on the basis of β-CD.
^{c} According to N$_2$ porosimetry and using a linearized BET model where the value for β-CD is 3.97 m^2/g.
^{d} Literature value (Ref. 5) for β-CD/EP at 1 : 22 mole ratio obtained from N$_2$ porosimetry.

between the carbon and hydrogen analyses in Table I, further spectroscopic and TGA characterization was carried out to further support the identity of the copolymer materials.

The 1 : 15 polymer had the greatest yield (cf. Table II) among the products studied and was observed to decrease in proportion to the cross linking density of the polymer. The differences in yield may be a result of the mass transfer between β-CD and EP because of the increased viscosity of the reactant mixture as the polymerization reaction proceeds. At higher EP mole ratios, the viscosity increases proportionately to the volume of EP added to the reaction mixture because the viscosity of EP is much higher as compared with water.[31]

The surface area increased slightly for the 1 : 15 and 1 : 25 materials at pH = 4.6 as compared with estimates obtained at pH = 10.3. This is further evidenced by greater sorption capacity at higher pH at 293 K, i.e. Q_m (pH 10.3) < Q_m (pH 4.6). The systematic difference in surface area (SA) estimates obtained from the dye-based method *vs.* the porosimetry estimates are related to hydration effects and the physical state of the polymer (i.e. anhydrous *vs.* hydrated forms). In aqueous solution, swelling of the polymer framework may occur for the solution conditions employed for the dye-based sorption; however,[32] no swelling is anticipated for nitrogen porosimetry measurements. The insoluble amorphous polymers are capable of adsorbing water and results in polymer swelling and morphology changes of the framework without dissolution.[5,28] Overall, the SA values of the polymeric materials range between 40.5 and 90.1 m^2/g, according to the dye-based method.

^{13}C NMR results

Figure 3 is a stack plot of ^{13}C NMR CP-MAS spectra for the three polymeric materials. There are four

main ^{13}C spectral lines observed for each of the polymers, similar to the spectra observed for β-CD hydrate (not shown). The ^{13}C NMR spectrum of β-CD (not shown) reveals four ^{13}C NMR lines between 60 and 110 ppm due to spectral overlap of some of the six carbon resonance lines of the seven α-D-glucose units. The spectral assignment reported for β-CD[33] agrees with the assignment reported in Figure 3 for the β-CD/EP copolymers. The difference between β-CD and its polymeric forms (cf. Fig. 3) are the broader ^{13}C resonance lines because of cross-linking with EP and the variable line intensity because of the amorphous character of each copolymer material. The broadening of the observed ^{13}C spectral lines for the nuclei of the β-CD/EP polymers occur because of the disordered nature of the materials resulting from the random substitution of EP at the various 21 hydroxyl sites for C_2—, C_3—, and C_6—) of β-CD. The increase in the ^{13}C line intensity ∼ 65 ppm (cf. asterisk in Fig. 3) for the 1 : 15, 1 : 25, and 1 : 35 copolymers is attributed to the spectral overlap of the ^{13}C signals for the methine and/or methylene groups of EP with those of β-CD at the coincident frequency. The ^{13}C NMR results in Figure 3 are in good agreement with the synthetic composition of β-CD and EP, and the previously reported NMR results for such β-CD copolymer materials.[29,34–36] The EP content of the copolymers are further corroborated from independent TGA results (*vide infra*).
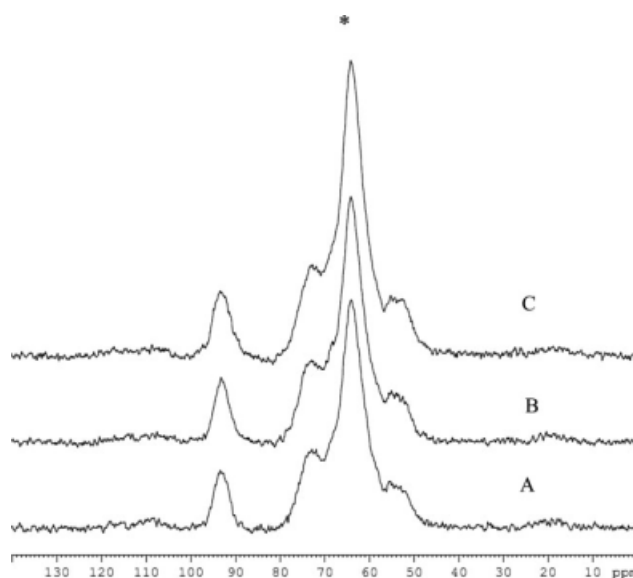

Figure 3 ^{13}C NMR CP-MAS spectra of the copolymer materials at three mole ratios; (A) 1 : 15, (B) 1 : 25, and (C) 1 : 35 β-CD/EP. The spectra were obtained using a 4 kHz spinning speed at a 90.554 MHz spectrometer frequency and 293 K. The chemical shifts were externally referenced to adamantane (δ = 38.56 ppm). The asterisk denotes the ^{13}C NMR resonance line of interest.

TGA and SEM results

TGA studies of each polymer were carried out to obtain estimates of the relative monomer composition of the copolymer materials. Figure 4(A–C) illustrates the first derivative plots [mass loss %/temperature (°C)] *vs.* temperature (°C) for each copolymer material. The relative peak area for each thermal event was deconvoluted using a Gaussian fitting function to obtain the individual peak areas. In general, there are two notable bands centered ~ 320 and 360°C, respectively. These two thermal events are related to mass losses from the decomposition of the copolymer as follows; (*i*) mass losses because of β-CD decomposition ~ 360°C,[24] and (*ii*) and decomposition of EP ~ 320°C. The peak area ~ 320°C increases as the EP content of the copolymer increases and varies according to the synthetic composition of the polymer. The differences in thermal stability of the EP domains are anticipated to vary with the crosslink density and the morphology of the copolymer material. The calculated monomer composition for β-CD and EP from the TGA results obtained in Figure 4 are in good agreement with the synthetic preparation of the materials.

Scanning electron microscope (SEM) images were obtained for each of the polymeric materials, as shown in Figure 5. The scaling depicted in Figure 5 is 10 μm and at this level of resolution, gross physical and morphological features of the copolymer materials may be compared. A detailed assessment of the copolymer micropore structure is not possible at this resolution; however, the framework appears dense and there are no apparent macropore (> 1 μm) features observed. The SEM results are consistent with the relatively low BET surface area estimates obtained from nitrogen porosimetry estimates (cf. Table II).

Sorption results

Porosimetry was used to investigate the surface area and pore structure properties of each of the copolymer materials. The surface area of the copolymers and native β-CD hydrate was estimated using the BET model and the corresponding values ranged between 40.5 and 90.1 m²/g (cf. Table II). The sorption properties of the copolymer materials were studied in aqueous solution at two different pH conditions, where PNP was used as the adsorbate molecule. Figure 6(A) illustrates the sorption isotherms at pH 4.6 and 22°C for the three copolymers. In general, the value of Q_e increases monotonically as the value of C_e increases. The "best fit" sorption parameters for the BET model[26,27] are listed in Table III. At pH 4.6, there are differences in the sorption capacity observed among the three materials for these
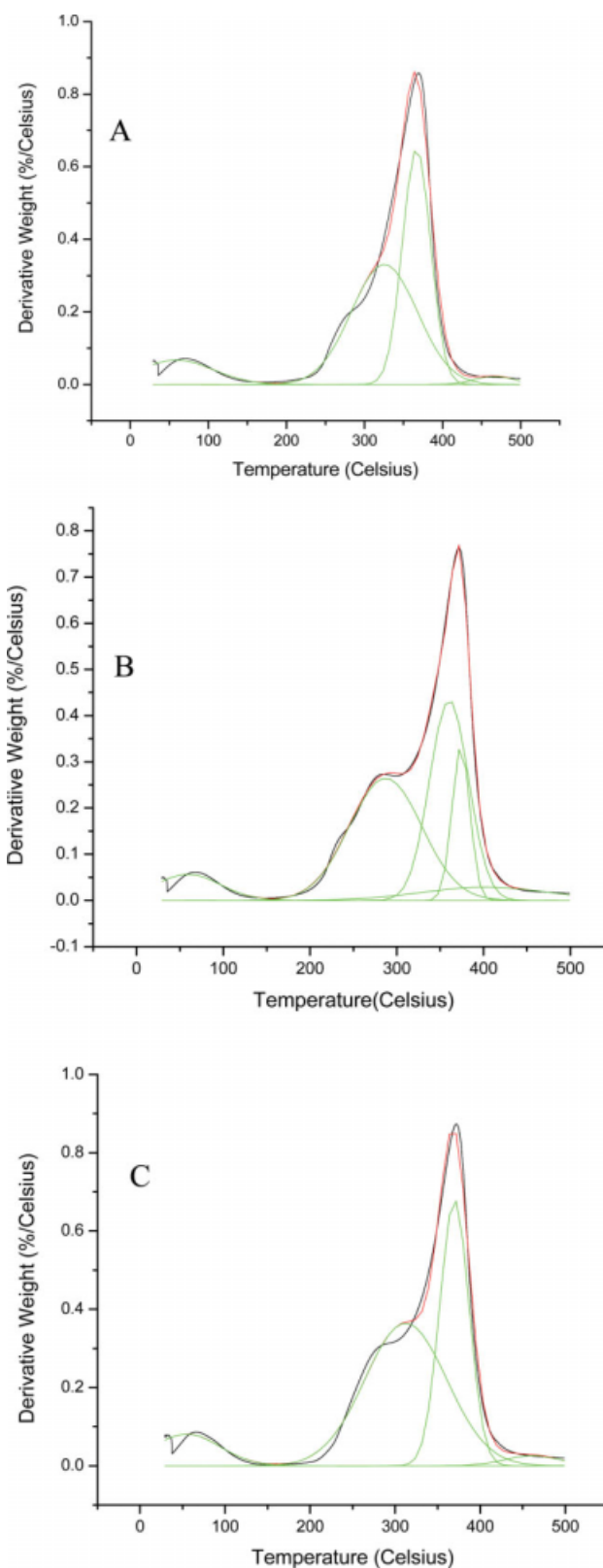

Figure 4 TGA results and calculated curves for monomer components; where A: β-CD/EP (1 : 15), B: β-CD/EP (1 : 25) and C: β-CD/EP (1 : 35) copolymer materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
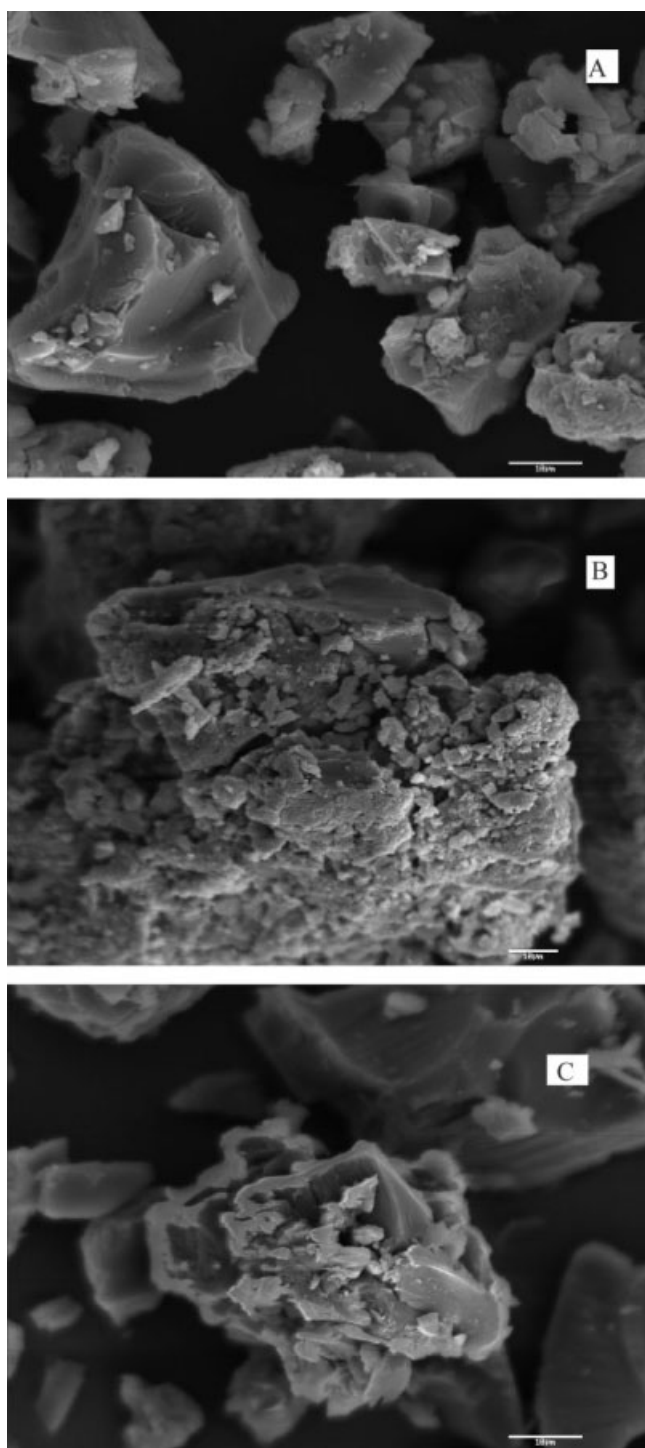
Figure 5 SEM images of β-CD/EP copolymers prepared at various mole ratios: A: 1 : 15, B: 1 : 25, and C: 1 : 35. The scaling in each micrograph are equivalent (scale bar = 10 μm) and the magnification is 1,200 times that of the real image.

Figure 6 Sorption isotherm for β-CD/EP copolymer materials with varying concentrations of PNP using a fixed mass of polymer (∼20 mg) at various conditions: A: pH 4.63 and 22°C, B: pH =10.3 and 22°C, and C: pH = 4.6 and 45°C. The best-fit results were obtained using nonlinear curve fitting with the BET isotherm model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sorption conditions, as follows: 1 : 35 > 1 : 25 > 1 : 15. The magnitude of Q_m tends to correlate with the increasing EP content of the copolymer material.

Figure 6(B) illustrates the sorption isotherm at pH 10.3 and 22°C for the three copolymers are similar to the results observed at pH = 4.6 [cf. Fig. 6(A)]. The
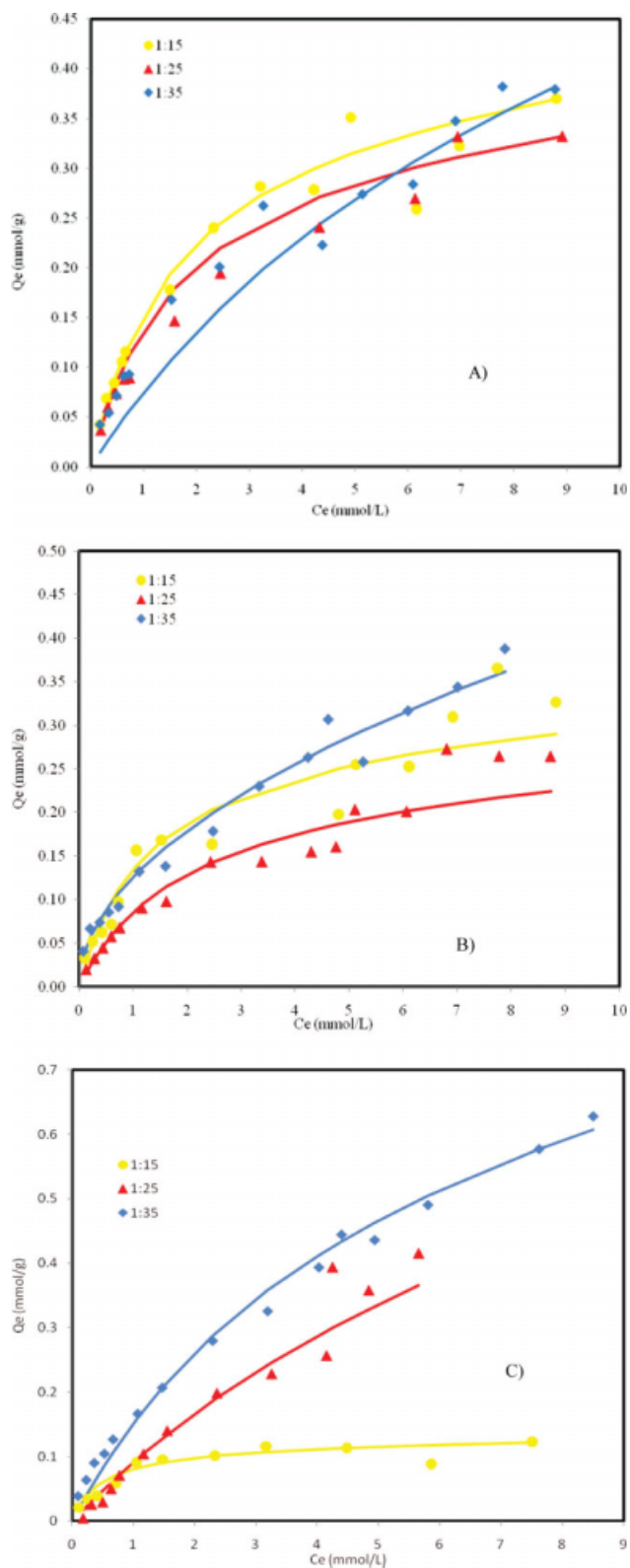
TABLE III
Best-Fit Parameter[/SUP]>[a,b] Estimates (Q_m, K_{bet}) Using the Bet Nonlinear Models at Various Temperatures and pH Conditions for the Sorption of PNP with β-CD/EP Polymers

Conditions	1:15 (β-CD/EP)	1:25 (β-CD/EP)	1:35 (β-CD/EP)
22°C and pH = 4.6	0.387[a], 56.6[b]	0.345[a], 57.5[b]	0.599[a], 12.4[b]
35°C and pH = 4.6	0.420[a], 74.0[b]	0.381[a], 39.8[b]	0.620[a], 26.7[b]
45°C and pH = 4.6	0.119[a], 184[b]	0.784[a], 11.4[b]	0.810[a], 20.0[b]
22°C and pH = 10.3	0.294[a], 72.4[b]	0.269[a], 38.0[b]	0.389[a], 42.7[b]

[a] Q_m (mmol/g).
[b] K_{BET} (Lmmol/g^2).

value of Q_e increases as the value of C_e increases for the 1 : 15 and 1 : 25 polymeric materials; however, the Q_e values are greater for the 1 : 35 copolymer. The increased sorption capacity observed for the 1 : 35 material at these conditions is attributed to its greater EP content and extensive cross link density. At pH = 10.3, the relative ordering of the sorption capacity is as follows: 1 : 35 > 1 : 25 ≈ 1:15.

Figure 6(C) illustrates the sorption isotherms at pH 4.6 and 45°C for the three copolymer materials. The relative ordering of the sorption capacity of each material at these conditions is given, as follows: 1 : 35 > 1 : 25 > 1 : 15. The sorption results are similar to those observed at lower temperatures (not shown) and the parameters are listed in Table III. The sorption capacity of each polymer increases as C_e increases according to the increasing EP content of each copolymer. The relative ordering of the sorption capacity at greater dye concentration depends on the temperature and pH conditions, as seen in Figure 6. At low values of C_e, the sorption capacities are similar up to C_e = 1 mmol/L and show greater dissimilarity thereafter. In general, the copolymer materials with increased EP content (crosslink density) are concluded to have greater sorption capacity and this is understood in terms of an increasingly microporous copolymer framework structure.

Isosteric heats of sorption

An analysis of the sorption isotherms (pH = 4.6) at various temperatures provide estimates of the enthalpy of adsorption, ΔH_{ads}, as a function of constant surface coverage [θ; cf. eq. (4)] as follows[37,38]

$$\left[\frac{\partial \ln K}{\partial T}\right]_\theta = \frac{\Delta H_{ads}}{RT^2} \qquad (5)$$

where the subscript (θ) implies that the fractional coverage is constant at these conditions. Application of the Gibbs–Helmholtz equation for these conditions provides a relationship for the determination of the isosteric heat of adsorption.

$$\left[\frac{\ln C_e}{1/T}\right]_\theta = \frac{-\Delta H_{iso}}{R} \qquad (6)$$

Isosteric enthalpy (ΔH_{iso}) is the enthalpy at the fixed surface coverage (θ) and is calculated by plotting the variable temperature sorption data according to eqn (6), where T is the temperature in Kelvin, R is the gas constant, C_e is the equilibrium concentration (mol/L) of the adsorbate in the aqueous phase.

Estimates of the isosteric heat (ΔH_{iso}) values were calculated for specific values of fractional surface coverage (θ = 0.01, 0.1, 0.25, and 0.50), according to eqn (6). The Q_m values were obtained from the BET model parameter estimates and the Q_e values from eqn (4). The C_e values were interpolated using a polynomial fit of the sorption data (i.e. Q_e versus C_e). For low values of θ, PNP is anticipated to be bound to sites with the most favorable interaction energies[35,36] such as the β-CD inclusion sites. The ΔH_{iso} values are exothermic (−13.6 to −14.9 kJ/mol) over the entire range of θ values for the 1 : 15 polymer; however, more negative values (ΔH_{iso} = −18.8 to −24.5 kJ/mol) are observed for the 1 : 25 polymeric material. At pH = 4.6, PNP is protonated and the ΔH_{iso} values are consistent with H-bonding and van der Waal's interactions.[39] It cannot be concluded that sorption occurs solely at either the interstitial or inclusion sites exclusively (cf. Scheme 1); however, previous studies have concluded that the inclusion of PNP within β-CD is favorable for these conditions.[7–9] There is greater sorption as the EP content of the polymer increases and this is attributed to synergistic effects related to the copolymer framework structure because of swelling and the occurrence of H-bonding between PNP and the EP domains of the polymer at pH = 4.6.

Removal efficiencies

The removal efficiencies (%P) of PNP from aqueous solution were calculated as follows:

$$\%P = \left(\frac{C_o - C_e}{C_o}\right) \times 100\% \qquad (7)$$

TABLE IV
Summary of the Removal Efficiencies (%P)[a] at Various pH and Temperature Conditions for a Fixed Mass (~20 mg) of β-CD/EP Polymeric Materials

pH Condition	4.6	4.6	4.6	10.3
Polymer Material	22°C	35°C	45°C	22°C
1 : 15	11–41%	13–50%	5–35%	10–47%
1 : 25	10–35%	10–30%	7–21%	8–30%
1 : 35	11–41%	15–45%	18–54%	12–58%

[a] The calculated range of values for %P correspond to a range of PNP concentrations ([PNP]$_o$ = 0.2 − 10 mM) and a fixed mass (~20 mg) of polymeric material.

where C_o and C_e are defined as aforementioned. The removal efficiencies depend on the pH, temperature, dye concentration, and both the amount and nature of the copolymer material.[5] In Table IV, the removal efficiencies tend to increase as the EP content of the copolymer increases for each isotherm. The % P values are greater at elevated pH and this is attributed to potential swelling of the framework because of electrostatic repulsions of the copolymer framework as partial deprotonation of the β-CD hydroxyl sites occur at pH = 10.3. The removal efficiencies tend to increase as the [PNP] decreases and this is understood in the context of a partition coefficient as a greater fraction of polymer bound adsorbate occurs when the relative mole ratio of β-CD exceeds that for PNP. Greater removal efficiencies ($\sim$ 58%) occur for polymers with increased cross linking density and possible swelling as the surface area of the polymer is predicted to increase as the EP domains increase in size, as concluded for "A-B$_n$ type" copolymers.[5,14,15]

The sorption of PNP cannot be unequivocally attributed to the formation of inclusion complexes with β-CD as there appears to be a synergistic role of EP in regard to the copolymer structure and sorption properties. The greater linker (EP) content increases the sorption capacity and the copolymer swellability, as well as changes to the hydrophile–lipophile balance of the copolymer.[10] Garcia-Zubiri et al.[40] reported uptakes for 1-naphthol by CD/epichlorohydrin copolymers and their estimates were greater for this type of adsorbate because of its apolar nature, as compared with PNP. The carbohydrate copolymer materials described in this work are versatile sorbents for the removal of PNP at millimolar concentration levels and exhibit good removal over the range of experimental conditions investigated.

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