

Sorption of Aromatic Compounds in Water Using Insoluble Cyclodextrin Polymers

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ABSTRACT: Insoluble β -cyclodextrin (β -CD) polymers have been used for the recovery of various organic pollutants from aqueous solutions. These resins have been prepared by polymerization using epichlorohydrin (Epi) as a crosslinking agent. Several cross-linked polymers with various degrees of β -CD were used. Several studies (time, concentration, kinetics, and pH) are presented here. The results show that these sorbents exhibit high sorption capacities toward substituted benzene derivatives. The mechanism of sorption is both physical adsorption in the polymer network and/or the formation of an inclusion complex and/or the formation of hydrophobic guest-guest interactions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1973–1978, 1998

INTRODUCTION

Benzene derivatives have been the subject of much interest in recent years^{1–8} because of increasingly stringent restrictions on the organic content of industrial effluents. These toxic compounds are the products of many industrial processes and they may be found in trace quantities in industrial waste water. Therefore, it would be advantageous to have adsorbent resins able to eliminate them. β -Cyclodextrin (β -CD) is a torus-shaped cyclic oligosaccharide made up of seven α -1,4-linked D-glucopyranose units with an internal hydrophobic cavity. It is well known that this structure gives rise to a remarkable capacity to

form inclusion complexes in solution or in the solid state with organic molecules, especially aromatics, through host-guest interactions. The association constants of the inclusion complexes depend on the size and polarity of the guest molecule and its shape.⁹ Hence, β -CD complexation is a procedure of choice for depollution techniques. In addition, insoluble polymers containing β -CD have the capacity to form inclusion complexes. We have previously reported some immobilization methods by which β -CD can be linked to silica beads¹⁰ and onto macroporous polymeric supports.¹¹ It was found that these materials exhibit high sorption capacities toward phenolic compounds.

In a recent work,¹ we proposed the use of insoluble β -CD polymers as a heterogeneous system to sorb dyes. Acid, direct, mordant, and reactive textile dyes were sorbed onto these synthesized polymers consisting of β -CD or hydroxypropyl- β -cyclodextrin (HP- β -CD) crosslinked by epichlorohydrin (Epi). The proposed mechanism for the

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Table I Experimental Conditions and Amount of β -CD Polymers Incorporated into the Materials

Polymer	Epi ^a	T (°C)	Time (h)	NaOHaq ^b	β -CD ^c
Polymer 1	10	50	2	50	290
Polymer 2	15	50	2	50	310
Polymer 3	17	50	5	23	700
Polymer 4	20	50	2	50	200
Polymer 5	20	50	24	50	420
Polymer 6	20	50	8	50	150
Polymer 7	30	80	2	50	110
Polymer 8	59	22	24	23	800

^a In molar ratio of Epi/CD.^b % in w/w.^c From spectrophotometric method, in mg/g.

sorption of dyes on polymers is both physical adsorption in the polymer network and/or the formation of a host-guest inclusion complex. In this article, we propose the use of the same β -CD polymers for the sorption of aromatic pollutants. The influence of several parameters (time, concentration, kinetics, and pH) on the sorption capacity of these insoluble polymers with respect to organic compounds is evaluated.

EXPERIMENTAL

Materials

β -CD supplied by Janssen Chimica (Beerse, Belgium) was recrystallized from water and dried overnight under vacuum at 100°C. Other compounds were purchased from various suppliers and were used without further purification.

Procedure for the Cyclodextrin Polymer

Insoluble polymers containing β -CD were prepared by polymerization in the presence of Epi as a crosslinking agent to obtain insoluble cyclodextrin polymers. Details of the materials and the synthetic procedure have already been described.¹ A series of polymers were prepared with different molar ratios of Epi/CD, temperature, time, and solvent. The experimental conditions are summarized in Table I. The materials used have different β -CD content (ranging from 20 to 80% w/w) as described in Table I.

Methods

The sorption capacities of the polymers were determined by the following two techniques. The first is the batch method. Fifteen mg of the sorbent was mixed with 5 mL of an aqueous solution of the pollutant compound (concentration $5 \cdot 10^{-4} M$) in a stopped flask that was shaken at room temperature. The residual concentration of the organic solute was determined by spectrophotometry and the sorption capacity calculated. All solutions were filtered before measurements ($0.47\text{-}\mu\text{m}$ Millipore filters). The second technique involved the use of open and recycling columns. For the open system, we used the following equipment: two tanks, one for the solvent and the other for the sample; a peristaltic pump; a two-way collector; a 1-mL column; and a fraction collector. The column was filled with 50 mg of polymer 4. Initially, the column was eluted using only water until the flow rate became constant. Then, a water solution containing the pollutant at the concentration of $5 \cdot 10^{-4} M$ was passed through the column for various times. For the recycling system column, the experimental conditions are the following: concentration of $5 \cdot 10^{-4} M$ in water for β -naphthol; flow rate of 1.5 mL/min; and a column filled with 50 mg of polymer 4 (8.8 μmol of β -CD). A fixed volume (10 mL) of the solution was eluted through the column many times over a period of about 400 min. The sorption capacity of the polymers in these two types of experiments were obtained by UV analysis of the eluted solutions at fixed times.

The sorption capacity of the polymers was investigated using phenol (P), *p*-nitrophenol (pNP), benzoic acid (BA), *p*-nitrobenzoic acid (pNBA), β -naphthol (BN), and chlorophenols (CIP) as model guest compounds. We also tested 4-*tert*-butylbenzoic acid (TBBA), because this compound, according to the high value of the association constant calculated by Wenz¹² by microcalorimetry, forms a very stable complex with β -CD in solution. Several parameters (time, concentration, kinetics, pH) were studied using polymer 4 which contained 200 mg of β -CD (176 μmol) per g of sorbent (see Table I).

RESULTS AND DISCUSSION

Batch Experiments

Kinetics of Pollutant Sorption

Figure 1 shows the sorption capacity of polymer 4 versus the stirring time toward different aromatic

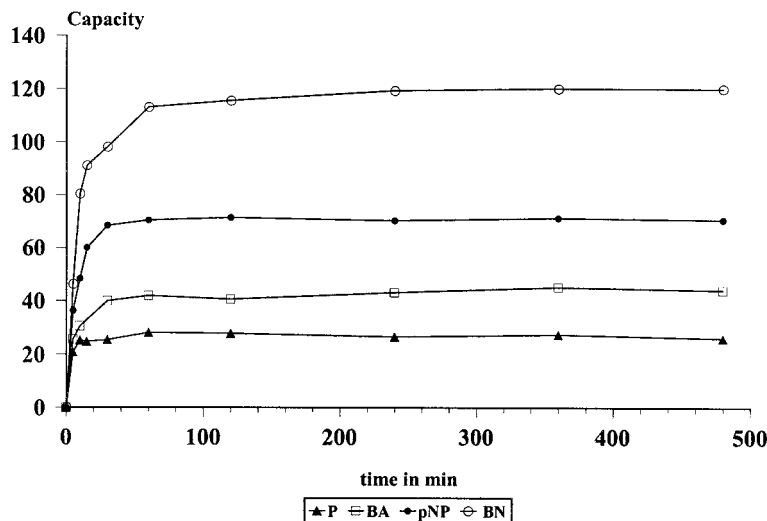


Figure 1 Kinetics of sorption capacity (in $\mu\text{mol/g}$) of several pollutants by the CD polymer (polymer 4; concentration $5 \cdot 10^{-4}$ mol/L).

compounds. The maximum capacity is obtained after 2 h for all the solutes studied. For the next experiments, 4 h is sufficient for reaching the plateau. The results also show that the order of the adsorption capacity for the pollutants examined in an aqueous solution with a starting concentration of $5 \cdot 10^{-4}$ M is the following: BN > pNP > BA > P. The sorption is much greater in the case of aromatic compounds which present compatible size, steric arrangement, and hydrophobicity with the β -CD: This point will be discussed later. In addition, it is well known that BN¹³ and pNP¹⁴ form stable complexes with β -CD; on the other hand, P⁹ forms a less stable inclusion complex. We found similar results with polymer 8 which contains 800 mg of β -CD per g of resin. The trend of the curves is the same and the quantity of each pollutant adsorbed is significant. We can assume that the formation of an inclusion complex is involved in the mechanism of sorption.

Figure 2 shows the sorption capacity of polymer 4 versus the starting concentration of pollutants using a contact time of 4 h. The quantity of the polymer was kept constant while the molar concentration of the guest molecule was varied between 10^{-5} and 10^{-3} M, corresponding to a molar ratio of guest/CD between 0.094 and 1.887. The quantity of the retained compound depends on the concentration of the aqueous solution. The trend of the curves reflects the affinity of the guest compound for the material. Using other polymers, we found similar trends for the curves. The sorption capacity increases with an increasing amount of β -CD.

TBBA was found to be insufficiently soluble in water at a concentration of $5 \cdot 10^{-4}$ M, and the comparison with the other compounds was carried out at $5 \cdot 10^{-5}$ M. The order of the sorption capacity for the pollutants (BN, pNP, P, and TBBA) examined in water with a starting concentration of $5 \cdot 10^{-5}$ M and 4 h of stirring time is the following: BN ($14.4 \mu\text{mol/g}$) > pNP ($9.3 \mu\text{mol/g}$) > TBBA ($7.7 \mu\text{mol/g}$) > P ($4.6 \mu\text{mol/g}$). The

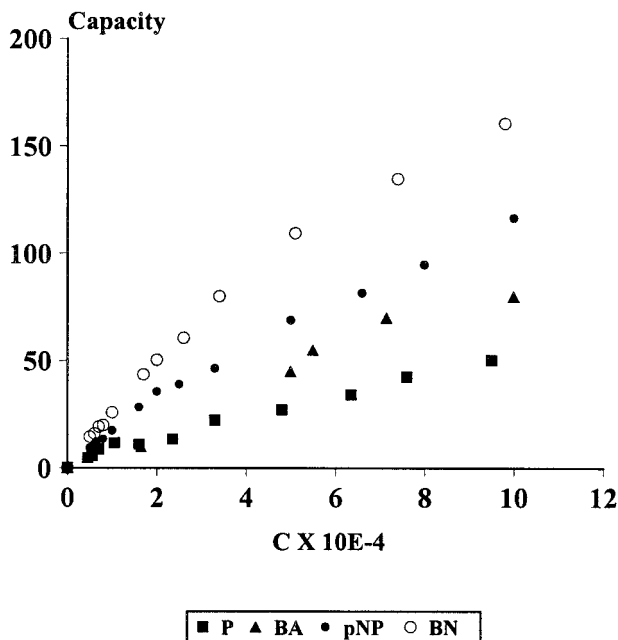


Figure 2 Capacity (in $\mu\text{mol/g}$) versus starting concentration of the pollutants in water (polymer 4; time 4 h).

value of the sorption capacity of TBBA is lower than that of pNP and BN although the association constant (K) between TBBA¹² ($K = 10^4 M^{-1}$) and β -CD is significantly higher than for pNP¹⁴ ($K = 1020 M^{-1}$) and BN¹³ ($K = 50 M^{-1}$ at pH 11). This can be explained by the fact that not only does β -CD play an important role in the sorption mechanism, but there are also other interactions, probably physical adsorption and/or hydrogen bond interactions, due to the crosslinked agent, and/or hydrophobic guest-guest interactions.

Influence of the pH on the Sorption Capacity

To evaluate the influence of the pH on the affinity of the pollutants for polymer 4 and to clarify the role of different factors which take place in the sorption mechanism, tests were carried out in buffer solutions at pH 2, 6, and 11. First, the influence of the pH on the sorption capacity of polymer 4 versus the starting concentration of the BN compound using a contact time of 4 h was studied (figure not shown). The range of concentration was between $5 \cdot 10^{-5}$ and $5 \cdot 10^{-4} M$. This guest was dissolved in each buffer solution. The trend of the curves are the same as those obtained in water. The quantity of the retained guest increases with the concentration of its buffer solutions. The results obtained at pH 2 and 6 and in water are very similar but are different from those obtained at pH 11, which show significantly weaker interactions. For example, the values of the sorption capacity for BN with a concentration of $5 \cdot 10^{-4} M$ are the following: 102, 107, 91, and 46 $\mu\text{mol/g}$ at pH 2 and 6, water, and pH 11, respectively. Similar results were obtained with pNP.

In Figure 3, we observe for all guest compounds an important decrease in the sorbed quantity at pH 11: This reflects the fact that the inclusion complex with β -CD and aromatic derivatives are less stable in basic than in neutral or acidic medium.⁹ We also note that in these basic conditions the decreasing order of their affinities is as follows: TBBA > 2,4,6 CIP > pNP > BN > pNBA > P > BA. The results found at pH 11 are in better agreement with the association constants between the guests and the β -CD than those in neutral water. On the other hand, we observe that at pH 2 and 6 the results are very similar to those obtained in water. These results can be explained by the different ionization degree of the guest upon the various pH used. It is interesting to note that an important increase of the sorption at pH 11 was observed for TBBA and the sorption capac-

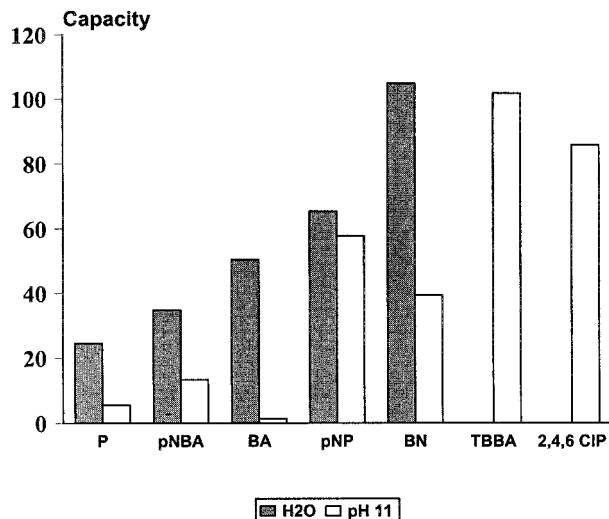


Figure 3 Comparison between sorption capacity (in $\mu\text{mol/g}$) of several pollutants by the CD polymer in water and at pH 11 (polymer 4; time 4 h; concentration $5 \cdot 10^{-4} \text{ mol/L}$).

ity was greater than that of BN. Other results obtained for 2,4,6-chlorophenol are similar to those of TBBA. Chlorophenols, insoluble molecules in water, exhibit high sorption at pH 11 using these systems.

Influence of the β -CD Content on the Sorption Capacity

The polymers can be divided in two groups: those having low (300 mg/g) and high (600 mg/g) β -CD content. Table II shows the influence of the β -CD content on the sorption capacity using several pollutants in water and at pH 11. These results show that the behavior of the first group (polymers 1, 2, and 4) of materials is similar and the very high sorption capacity in water does not seem to be correlated with the quantity of β -CD. For example, we found for the first group a sorption capacity for pNP and BN of about 66 and 105 $\mu\text{mol/g}$, respectively. The second group (polymers 3 and 8) show a sorption capacity which seems to better reflect the possible association constants of the complexes between the β -CD and the guest. For BN, we found 70 $\mu\text{mol/g}$ using polymer 8 (800 mg of β -CD per g) and 120 $\mu\text{mol/g}$ using polymer 3 (700 mg of β -CD per g), and for pNP, we found 91 $\mu\text{mol/g}$ using polymer 8 and 63 $\mu\text{mol/g}$ using polymer 3: This can be explained by more extensive reticulation in polymer 8 than in polymer 3 or by minor physical adsorption due to the polymer network introduced by the Epi. Figure 4 shows

Table II Influence of β -CD Content on the Sorption Capacity (in $\mu\text{mol/g}$) of Several Compounds by CD Polymers in Water and at pH 11 (Time 4 h)

Polymers	β -CD ^a	P ^b	pNP ^b	BN ^b	CIP ^c	2,4CIP ^c	2,4,6CIP ^c
Polymer 4	176	24.5	65.5	105.0	41.6	28.9	31.9
Polymer 1	255	24.6	60.0	104.3	55.3	32.1	38.5
Polymer 2	273	26	66	106.2	19.5	30.8	32.8
Polymer 3	617	43.4	63.0	120.0	20.9	62.8	68.5
Polymer 8	705	32.2	91.0	170.0	16.6	53.5	62.5

^a In $\mu\text{mol/g}$.^b In water; concentration $5 \cdot 10^{-4}M$.^c At pH 11; concentration $1.5 \cdot 10^{-4}M$.

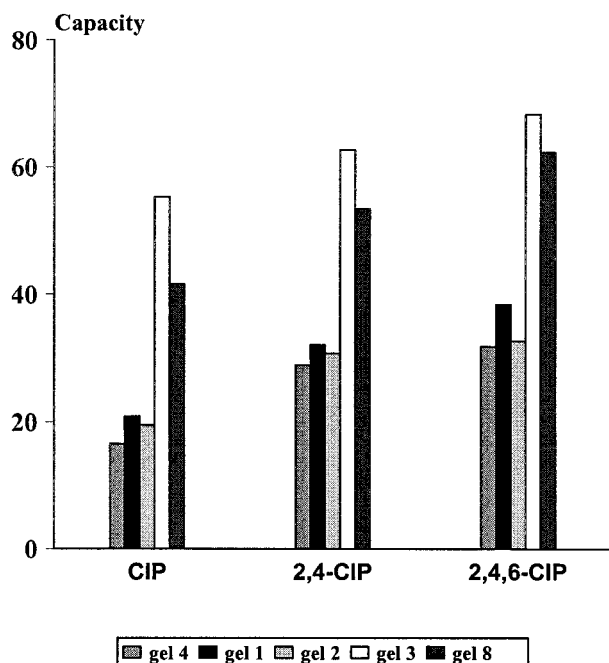
that the sorption capacity for the chlorophenolic compounds at pH 11 increases with the amount of β -CD present in the different polymers. This confirms the fact that in this case the action of β -CD is predominant.

Column Setup

In a second kind of experiment, we used open and recycling columns. We tried to saturate the polymer using a significant amount of solution containing the aromatic compound. The aim was to confirm that not only does β -CD play a role in the sorption, but so also does the polymer network

introduced by Epi. In this study, we present only the results obtained using BN. As described above, this compound exhibits the best interaction with these sorbents. The sorption capacity of the polymer was found to be independent of the flow rate used in the range between 1 and 2.5 mL/min. Table III shows that when the elution time increases the amount of BN adsorbed increases, as expected. It is interesting to note that the quantity sorbed is always higher than the content of β -CD (176 μmol per g of polymer) present. This is a confirmation that the material participates in the complexation. This excess can also be explained by the presence of guest-guest (hydrophobic) interactions which cause an accumulation of the pollutant at the surface of the resin. It is possible in this case to regenerate the polymer using several washes with water, but we observed that only 30% of the adsorbed BN was removed whatever the quantity of water used. This is another confirmation of the existence of strong interactions between BN and the polymer network. For the complete regeneration of the material, it is necessary to use a mixture of water and ethanol.

For the recycling columns, we used different amounts of polymer 4 with the intention to obtain different ratios between β -CD and the amount of

**Figure 4** Influence of the β -CD content on the sorption capacity (in $\mu\text{mol/g}$) of chlorophenols by CD polymers at pH 11 (time 4 h; concentration 10^{-4} mol/L).**Table III** Evaluation of Sorption Capacity by Polymer Using an Open Column

Elution Time ^a	Amount of BN Eluted ^b	Amount of BN Adsorbed ^b
60	900	380
120	1800	460
180	2700	580

^a In min.^b In μmol per g of sorbent.

Table IV Evaluation of Sorption Capacity by Polymer Using a Continuous Column

BN/CD ^a	Polymer ^b	Amount of BN Eluted ^c	Amount of BN Sorbed ^c	% R ^d
0.5/1	56.75	88	72	82
1/1	28.37	176	137	78
2/1	14.19	352	295	83

^a Molar ratio.^b In mg of sorbent.^c In μmol per g of sorbent.^d R for the ratio between BN sorbed and BN eluted.

BN present in the solution. Table IV shows the amount of BN adsorbed for 1 g of sorbent. This experiment is analogous to that which was made batchwise where the amount of the guest adsorbed increases as a function of the increase of the guest concentration. The results show that when we change the molar ratio between BN/CD the percentage of the adsorbed BN is almost constant (R about 80% in Table III). More experiments will be carried out using column techniques.

CONCLUSION

Adsorbents made from insoluble β -CD polymers possess specific inclusion recognition capabilities with aromatic compounds. The results indicate that these materials are high-capacity adsorbents for the recovery of organic pollutants. The inclusion complex formation resulting from the presence of β -CD and the physical adsorption due to the polymer network introduced by the Epi are combined in the sorption mechanism. There is also the presence of hydrophobic guest-guest interactions. The results presented are in agreement with preliminary literature data published by Szejtli and coworkers.¹⁵⁻¹⁷ Our next objective will be to find the relationship between their retention behavior and molecular structure. The results presented could be correlated with those obtained in another work.¹⁸ Indeed, these β -CD polymers have been characterized using NMR solid-state techniques. We found that in the materials there are two kinds of components, cross-linked β -CD and polymerized Epi, which have two different molecular mobilities. This could explain

the fact that the sorption mechanism involves both inclusion complex formation and physical adsorption.

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