Sorption Properties Toward Substituted Phenolic Derivatives in Water Using Macroporous Polyamines Containing β -Cyclodextrin

GRÉGORIO CRINI,¹ LUDOVIC JANUS,² MICHEL MORCELLET,² GIANGIACOMO TORRI,³ NADIA MORIN⁴

¹ Centre de Spectrométrie, Université de Franche-Comté, 16, Route de Gray, 25000 Besançon, France

² Laboratoire de Chimie Macromoléculaire, UA CNRS 351, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

³ Istituto Scientifico di Chimica e Biochimica "G. Ronzoni," 81 Via G. Colombo, 20133 Milano, Italy

⁴ Laboratoire de Chimie Physique et Minérale, Faculté de Médecine et de Pharmacie, Place Saint Jacques, 25030 Besançon Cedex, France

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ABSTRACT: Macroporous polyamines containing β -cyclodextrin (β -CD) are used for the recovery of various organic pollutants from aqueous solutions. Several insoluble polyamines with various degrees of β -CD were prepared. Studies concerning the sorption kinetics, the effect of pollutant concentration, pH of the solutions, and β -CD content are presented here. The results of sorption experiments show that these sorbents exhibit high sorption capacities toward substituted phenolic derivatives. The mechanism of sorption is both physical adsorption in the resin polymer network through acid-base interactions, ion exchange, and hydrogen bonding due to the amino groups and the formation of an inclusion complex due to the β -CD molecules through host-guest interactions, and hydrophobic interactions such as guest-guest interactions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2903–2910, 1999

Key words: capacity sorption; substituted phenolic derivatives; macroporous polyamines; β -cyclodextrin

INTRODUCTION

Environmental aspects of aromatic compounds in particular, substituted phenolic derivatives have become increasingly important in recent years as a result of stringent restrictions on the organic content of industrial effluents.¹⁻⁹ These toxic compounds result from many industrial processes, and they are common water pollutants. Therefore, it is necessary to have sorbents that are able to eliminate them.^{1-4,7,10} The sorption of compounds using crosslinked polymers containing grafted ligands is one of the reported methods for the removal of such pollutants even in low concentrations. It is well known that β -cyclodextrin (cyclomaltoheptaose or β -CD), which possesses a hydrophobic cavity, gives rise to a remarkable ability to form inclusion complexes in solution with organic molecules, especially phenolic derivatives, through host–guest interactions.^{11–16} Hence, β -CD complexation is a very good procedure for wastewater treatment.^{1–3,7}

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The results obtained for the sorption capacity in terms of efficiency and selectivity can be explained by different mechanism including acidbase interaction, hydrophobic interaction, and inclusion complex formation.

In a recent work,¹⁷ we prepared new organic sorbents based on macroporous polyamine beads containing β -CD. These polymers, which are insoluble in water and in organic solvents, have been prepared by suspension copolymerization using divinylbenzene as crosslinking agent. These copolymers contain reactive primary amino groups that were used for the functionalization by β -CD. In order to obtain beads with a high degree of β -CD, maximum accessibility of the β -CD cavity and high specific areas, several factors (reaction time, amounts of the reactants, composition of solvent and temperature) were varied. Several supports with various degrees of substitution by β -CD were synthesized. These supports were also characterized using solid state nuclear magnetic resonance spectroscopy (cross-polarization magic angle spinning NMR).

In this paper, we describe the complexing properties of these insoluble polyamines toward organic pollutants using the batch method. The influence of several parameters (kinetics of sorption, i.e., contact time, effect of the pollutant concentration, pH of the solution, and β -CD content) on the sorption capacity of these porous organic polymers with respect to organic compounds is evaluated. The results of sorption experiments are reported.

EXPERIMENTAL

Procedure and Materials

The macroporous polyamines containing β -CD have been prepared in three steps: (1) suspension copolymerization between styrene and a vinylamine monomer precursor (N-vinyl-t-butyl carbamate) using divinylbenzene as crosslinking agent, (2) solvolysis of the carbamate protecting groups, and (3) functionalization of the free primary amino groups by β -CD. Details of the materials and the synthetic procedure had already been described.¹⁷ A series of sorbents were used, having different β -CD contents (ranging from 90 to 430 μ mol per gram of resin) as described in Table I. The method used for the determination of the amount of β -CD immobilized onto the beads has been the determination of reducing sugars with tetrazolium blue, as described earlier.¹⁸

Table I	Characteristics of the Resins
Containi	ng β-CD

Resin	$\beta ext{-}\mathrm{CD}^{\mathrm{a}}$	S ^b
Ι	0	85
II	89	62
III	109	95
IV	163	65
V	184	53
VI	242	53
VII	319	89
VIII	432	50

^a Determined from the tetrazolium blue spectrophotometric method in μ mol/g.

 $^{\rm b}$ Specific surface area in m²/g as determined by the BET method. 17

Methods

The sorption capacities of the insoluble beads have been evaluated using the batch method. Typically, 20 mg of resin are added to 5 mL of an aqueous solution of aromatic compound at known concentration in a tightly closed flask. The solution is then stirred on a rotating shaker at room temperature. Preliminary kinetic experiments had shown that 120 min contact time was sufficient for an equilibrium to be reached. The sorbent is removed by centrifugation or filtration before measurements. The residual concentration of the organic solute is measured by spectrophotometry and the sorption capacity calculated. The results are reported in µmol/g of beads. The sorption capacity is investigated using phenol (P), mnitrophenol (mNP), o-nitrophenol (oNP), p-nitrophenol (pNP), chlorophenol (ClP), 2,4-dichlorophenol (2,4ClP), and 2,4,6-trichlorophenol (2,4,6ClP) as model guest solutes.

RESULTS AND DISCUSSION

Kinetics of Capacity Sorption

Figure 1 shows the sorption capacity of resin I (no β -CD) and resin VIII (containing 432 μ mol β -CD/g of beads) vs stirring time in water and at pH 11 toward the oNP compound. The kinetics of sorption are fast and the maximum capacity is obtained after 1 h. For the next experiments, 2 h will be sufficient for reaching the plateau. The beads without β -CD exhibit rather high sorption capacities [Figures 1(a) and 1(b)]: in this case, the capacity of sorption is based only on the presence of acid–base interactions, ion exchange, and hy-

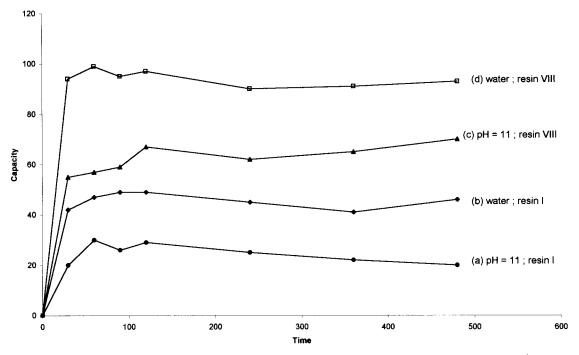


Figure 1 Kinetics of sorption capacity (in μ mol/g) of oNP at concentration $5 \cdot 10^{-4}$ mol/L, in water and at pH 11 using resins I and VIII (time in min).

drogen bonding between the amino groups of the polymer network and the oNP solute. That the sorption capacity decreases at pH 11 when oNP is ionized emphasizes the role of the interactions between the hydroxyl groups of oNP and the amino groups of the polymer. When the resin contains β -CD molecules [Figures 1(c) and 1(d)], an important increase of the sorption capacity due to host-guest interactions is observed. This shows that β -CD molecules contribute to the sorption mechanism through inclusion complex formation. If the results are expressed as a function of the surface area of resin (capacity in μ mol/m²), the capacity is multiplied by a factor 6 in presence of β -CD. With the β -CD resins, the tests have also been carried out in buffer solutions at pH 11. In addition, in this case, an important decrease of the sorption capacity is obtained, nearly equal to the one observed in pure water. We have found similar results using others solutes.

Figure 2 shows the sorption capacity of resins I and VIII vs stirring time at pH 11 toward *p*chlorophenol (pClP), *m*-chlorophenol (mClP), and 2,4,6ClP compounds. The kinetics of sorption are very fast and the beads without β -CD exhibit rather low but significant sorption capacities [Figures 2(a), 2(b), and 2(c)]. When the resin contains β -CD molecules, a significant increase of the sorption capacity is observed [Figures 2(d), 2(e), and 2(f)]. This confirms that β -CD plays an important role in the sorption mechanism. This effect is more important in the case of mClP solute. Using these first results, we can assume that the formation of an inclusion complex due to the β -CD molecules and the presence of other interactions such as acid-base interaction, hydrogen bonding due to the amino groups of the polyamine, and physical surface adsorption are involved in the mechanism of sorption.

In Figures 3 and 4, the comparison between the sorption capacities of several compounds by resins I, II, and VIII in water and at pH 11 is represented. The results in Figure 3 for resin I (no β -CD) indicates the interaction of some phenolic derivatives with the polyamine matrix: the sorption capacity for these pollutants examined in water (starting concentration of $5 \cdot 10^{-4}M$) is in the following order: pNP > oNP > mNP > P. Thus, the sorption capacity depends on the position of the substituents and also on the pK values of the different isomers (meta: 8.28; ortho: 7.17; para: 7.15). Among the three disubstituted compounds, the meta derivative, which is the more basic, presents the lowest interaction with the polyamine network. With resins IV and VIII, the best results are still for the pNP isomer, which gives the most stable complex with β -CD and the most important interactions with the polyamine

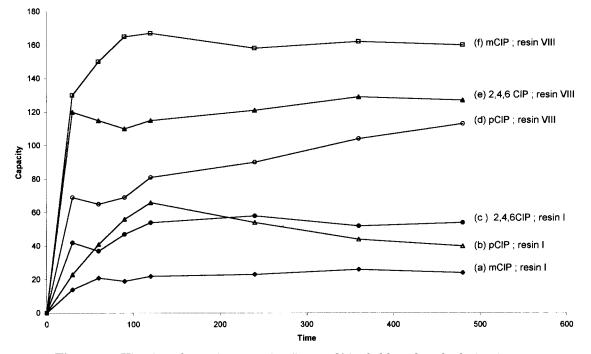


Figure 2 Kinetics of sorption capacity (in μ mol/g) of chlorophenols derivatives at concentration $5 \cdot 10^{-4}$ mol/L by resins I and VIII at pH 11 (time in min).

matrix. The pNP compound presents the most compatible size and steric arrangement with the β -CD cavity.¹¹⁻¹⁴ Literature data confirm that *p*-

nitrophenol^{19,20} forms stable inclusion complexes with β -CD, while on the other hand, phenol^{11,21} forms a less stable complex. Thus, it seems rather

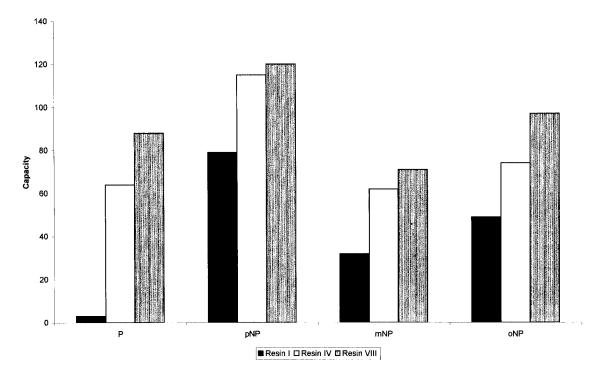


Figure 3 Comparison between sorption capacity (in μ mol/g) of several compounds in water by resins I, IV, and VIII (time 2 h; concentration 5 \cdot 10⁻⁴ mol/L).

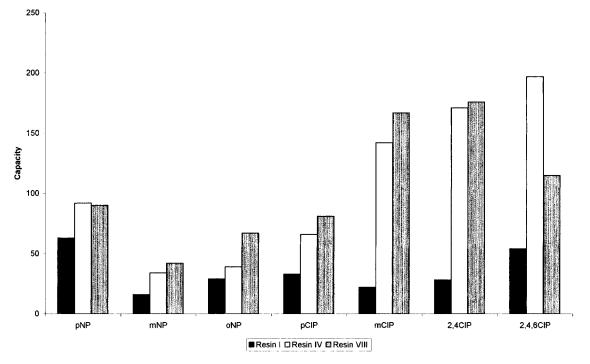


Figure 4 Comparison between sorption capacity (in μ mol/g) of several compounds at pH 11 by resins I, IV, and VIII (time 2 h; concentration $5 \cdot 10^{-4}$ mol/L).

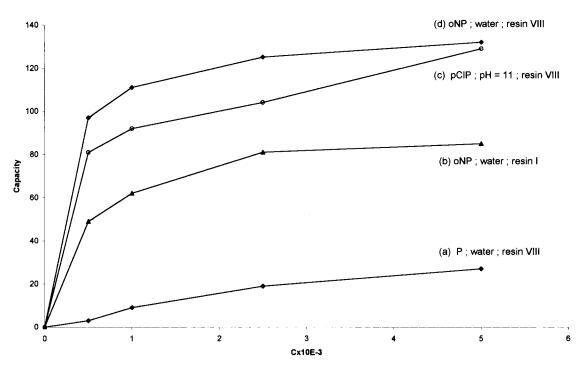


Figure 5 Capacity (in μ mol/g) vs starting concentration of solute in water and at pH 11 using resins I and VIII (time 2 h).

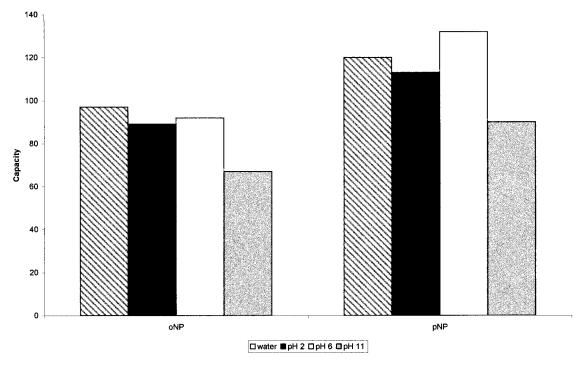


Figure 6 Influence of the pH on the sorption capacity (in μ mol/g) of oNP and pNP compounds at pH 2, 6, and 11, and in water (resin VIII; time 2 h; concentration $5 \cdot 10^{-4}$ mol/L).

surprising that the higher capacity increase when going from resin I to resin IV or VIII is for phenol. In addition, the capacity increase for the four pollutants in Figure 3 when going from resin IV to resin VIII is not in relation with the increase of β -CD content. This could indicate steric restric-

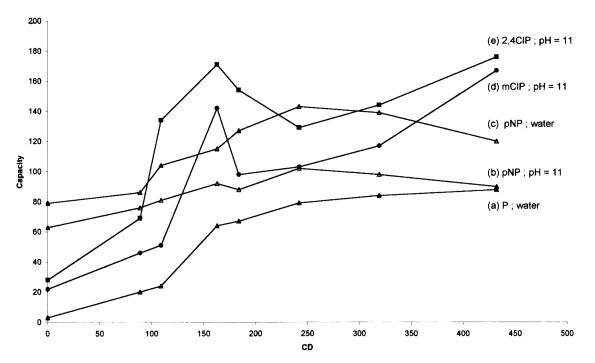


Figure 7 Influence of the amount of β -CD on the sorption capacity (in μ mol/g) (time 2 h; concentration $5 \cdot 10^{-4}$ mol/L).

tions for the accessibility of the β -CD cavity at high degree of functionalization. The decrease of the specific surface area could also contribute since a part of the sorption capacity seems to depend on physical adsorption.

Chlorophenols, in particular 2,4,6-trichlorophenol, exhibit also high sorption at pH 11 using these beads (Fig. 4). In these basic conditions, the order of their affinities is as follows: 2,4,6ClP > 2,4ClP > mClP > pNP > pClP > oNP > mNP. We observe for the nitrophenol isomers a significant decrease in the sorbed quantity at pH 1: this reflects the fact that the interaction with the amine group of the matrix is lower as said above and also that the inclusion complexes of β -CD and phenolic derivatives are less stable at this pH than in water.¹⁰ For phenol, the sorption capacity at pH 11 is nearly zero.

Influence of the Starting Concentration on the Sorption Capacity

Figure 5 shows the sorption capacity of resins I and VIII vs starting concentration of oNP, pClP, and P solutes using a contact time of 2 h. The quantity of resin has been kept constant while the molar concentration of the solute has ranged from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}M$. For concentrations over $5 \cdot 10^{-3}M$, some problems of solubility were encountered. The results show that the sorbed quantity increases with an increase of the starting concentration up to $5 \cdot 10^{-3}M$ and then reaches a plateau. The quantity of oNP solute adsorbed by the resin without β -CD is also presented in Figure 5(b). Here again, the capacity increases with concentration and confirms strong interactions between the solute and the polymer network.

Influence of the pH on the Sorption Capacity

To evaluate the influence of the pH on the affinity of the pollutants and to clarify the role of the different interactions that take place in the sorption mechanism, tests were carried out in buffer solutions at pH 2, 6, and 11 in addition to water (Fig. 6). The values of the sorption capacity for oNP are: 89, 92, 67, and 97 μ mol/g, respectively. The results obtained at pH 2 and 6, and in water, are very similar, but are significantly higher than those obtained at pH 11. These results can be explained by the different degrees of ionization of the solute with the various pH used. Similar results are obtained with pNP. The influence of the pH on the sorption capacity vs the concentration of oNP solute was studied (not shown). The trend of the curves at pH 2 and 6 are the same as those obtained in water (see Fig. 5).

Influence of the Amount of β -CD on the Sorption Capacity

Figure 7 shows the influence of the amount of β -CD on the sorption capacity of resins in water and at pH 11 toward the pNP, mClP, and 2,4ClP compounds. As expected, the overall trend is an increase of the sorption capacity with increasing amounts of β -CD, corresponding to increasing interactions between β -CD and the solutes. The trend of the curves reflects the affinity of the guest solute for the β -CD molecules. This clearly indicates that, apart from the interactions of the solute with the amino groups of the bead, the inclusion phenomenon plays the major role. This is especially clear for phenol, which does not interact with the matrix (the capacity of resin I is very low). The experimental values of the capacities are always lower than the theoretical ones, expressed on the basis of the β -CD content by assuming a 1:1 stoichiometry for the inclusion complex. For example, the capacity of resin VIII should reach at least 400 μ mol/g. This difference indicates, as suggested earlier, some steric restrictions for the access of the solute to the β -CD cavity.

CONCLUSION

In this paper, some results, obtained using macroporous polyamines containing β -CD, were presented. These adsorbents have been used for the recovery of various organic pollutants from aqueous solutions. They possess specific inclusion recognition capabilities toward aromatic compounds through an inclusion process. The proposed sorption mechanism involves several kinds of interactions: acid-base interactions and hydrogen bonding due to the polyamine network, interactions due to the formation of an inclusion complex with β -CD molecule. All these interactions play an important role in the mechanism of sorption.

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