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Adsorption of Bisphenol A by Cross-Linked β-Cyclodextrin Polymer

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Abstract

An insolubilized β-cyclodextrin derivative (polyCD) was prepared by polymerizing cyclodextrin with epichlrohydrine. By stirring 5 mg/ml of polyCD in 0.2 mM bisphenol A (BPA) solution at pH 7.0 for 2 h, more than 98% of BPA was adsorbed on polyCD. The capacity of the adsorption was determined to be 84 mg-BPA/g-polyCD, meaning 0.65 mol-BPA/mol-CD (in polyCD). The effect of pH on the adsorption was studied and found that BPA was effectively adsorbed on polyCD at pH between pH 2.2–9.1, but the efficiency decreased at pH 10.8, suggesting that it did not adsorb the BPA anion. The polyCD did not adsorb aromatic amino acids, indicating that BPA could selectively be removed from a solution containing amino acids.

Introduction

Bisphenol A (BPA) is the compound used as the raw material of polycarbonate and epoxy resins. It is also used as a plasticizer of polyesters. Recently, BPA has been listed among possible endocrine disrupters by EPA (http://www.ergweb.com/endocrine/), because it is suspected of having an estrogen-like effect at very a low dose [1–4]. Considering the safety of foods, the elution of BPA from polycarbonate tableware is of concern. Thus it is worth trying to develop a method to remove possible contamination of BPA from foods.

It is well known that cyclodextrins form host-guest complexes with hydrophobic compounds. This phenomenon leads to the idea that insolubilized cyclodextrin may act as a good adsorbent of BPA. If such cyclodextrin derivatives adsorb BPA, it will be a good method to remove BPA from liquid foods because the insoluble polymer will be easy to remove from liquid.

In this report, we describe the possibility of the removal of BPA from food by using an insoluble highly-crosslinked β-cyclodextrin polymer.

Experimental

Cross-linked cyclodextrin

An insoluble derivative of β-cyclodextrin was prepared as previously described [5] with some modification. β-Cyclodextrin (20 g) was dissolved in 25% (wt/wt) aqueous NaOH solution, followed by dropwise addition of epichlorohydrine (20 g) at 50 °C with stirring. Gel formed within 20 min and the reaction mixture was kept at 50 °C for 2 h to complete the reaction. The gel formed was washed consecutively with acetone and water, crashed into 0.1–0.5 mm (diameter), followed by drying in vacuum oven at 50 °C overnight. Finally, 26.4 g of the cross-linked β-cyclodextrin polymer (polyCD) were obtained (yield 70%).

Adsorption by polyCD

The standard conditions of the adsorption by polyCD were carried out as described below. To a solution of 0.2 mM BPA in 20 mM MOPS buffer (pH 7.0), polyCD was added and the solution was kept stirring at 20 °C for 1 h. Then, polyCD was removed by centrifuge and the concentration of BPA was determined by measuring Abs_{293} after mixing the supernatant with the equivolume of 1 M Na_2CO_3. Adsorptions of L-tyrosine, L-tryptophan were also examined by substituting BPA to each of them. Concentrations of L-tyrosine and L-tryptophan were determined by the same method as BPA.

Results

Adsorption OB BPA by polyC

When 1-10 mg of polyCD was added to the 0.2 mM BPA solution at pH 7.0, the concentrations of BPA after 1 h adsorption were measured. As shown in Figure 1, the concentration of BPA in the supernatant decreased. Using 5 mg of polyCD, the concentration of BPA was less than 0.05 mM, indicating that more than 98% of BPA was adsorbed on polyCD. Time course of the adsorption was traced as shown in Figure 2. Using 1 mg/ml of polyCD, 92% and 97% of BPA was adsorbed after 2 h and 18 h, respectively.

To measure the adsorption capacity of polyCD, 1 mg of polyCD was added in 10 ml of 0.2 mM BPA solution

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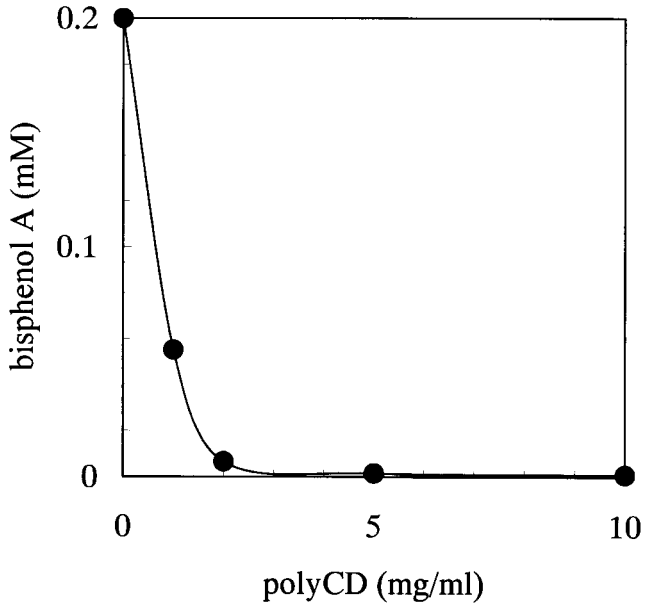

Figure 1. Effect of the amount of polyCD on the adsorption of BPA. Initial concentration of BPA, 0.2 mM; 20 mM MOPS-Na buffer (pH 7.0), 20°C, 1 h.

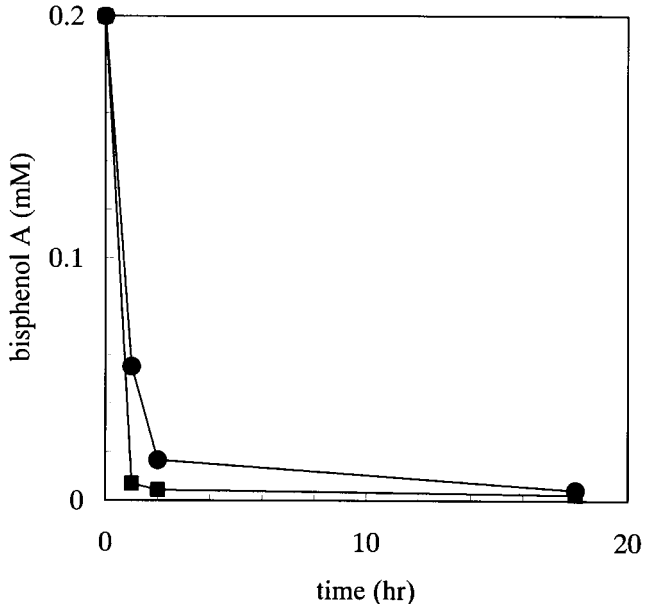

Figure 2. Time course of the adsorption of BPA. (circle), 1 mg/ml polyCD; (square), 2 mg/ml polyCD. Initial concentration of BPA, 0.2 mM; 20 mM MOPS-Na buffer (pH 7.0), 20 °C.

at pH 7.0, and the solution was stirred for 18 h at 20 °C. The concentration of BPA was 0.163 mM suggesting that 1 mg of polyCD adsorbed 370 nmol of BPA (84 μg-BPA/mg-polyCD). The ratio of BPA adsorbed against β-cyclodextrin residue in polyCD was estimated to be 0.64, based on the data that 1 mg of polyCD contained 580 nmol of β-cyclodextrin calculated by measuring the total carbohydrate in polyCD employing the phenol-sulfuric acid method [6].

Effect of pH on the adsorption was measured using the following buffers; 20 mM citrate-Na (pH 2.2 and 3.2), 20 mM acetate-Na (pH 5.2), 20 mM MOPS (pH 7.0), 20 mM CHES (pH 9.1), and 20 mM CAPS (pH 10.9). As shown in Figure 3, the adsorption was stable in the pH range from

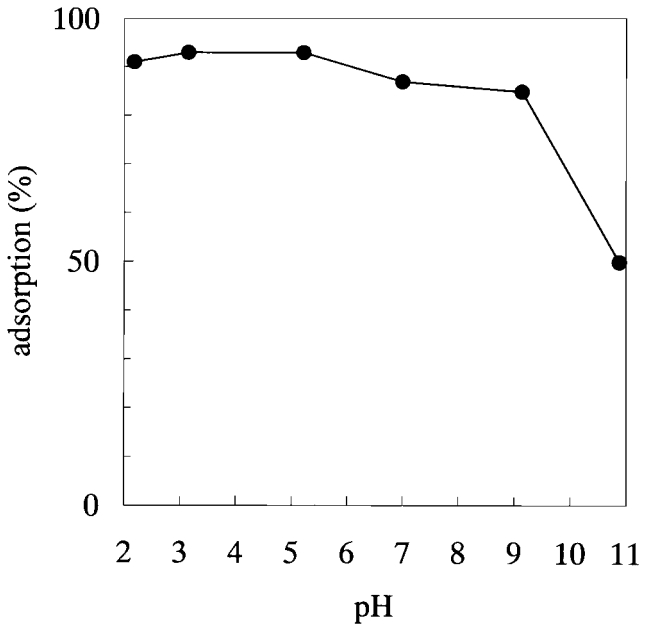

Figure 3. Effect of pH on the adsorption. Initial concentration of BPA, 0.2 mM; polyCD, 1 mg/ml; 20 mM MOPS-Na buffer (pH 7.0), 20 °C, 1 h.

Table 1. Adsorption of hydrophobic amino acids by polyCD

polyCD (mg/ml)	L-tyrosine (mM)	L-tryptophan (mM)	BPA (mM)
0	0.200	0.200	0.200
1	0.201	0.198	0.055
2	0.201	0.197	0.007
5	0.201	0.195	0.002
10	0.200	0.188	0.001

From 0.2 mM of each compound, 20 mM MOPS-Na buffer (pH 7.0), 20 °C, 1 h.

acidic to neutral but the efficiency decreased at pH 10.9. It suggests that the ionization of BPA caused the deficiency because the pKa of BPA was estimated around 10.

Adsorption of hydrophobic amino acids by polyCD

Adsorptions of 0.2 mM L-tyrosine and L-tryptophan with 1–10 mg/ml polyCD were examined. As shown in Table 1, no adsorption of L-tyrosine was observed. A small decrease in the concentration of L-tryptophan was observed, but the efficiency of the adsorption was much less than BPA.

Discussion

In this report, the authors are pursuing a method to remove BPA possibly contaminated in foods. We synthesized polyCD, a β-cyclodextrin polymer highly cross-linked by epichlorohydrine. The polymer was insoluble and it adsorbed BPA as expected. The efficiency of the adsorption was as good as 65% of the β-cyclodextrin residues in polyCD participated in the adsorption. The adsorption was stable at acidic and neutral conditions. This is advantageous for our purpose because the pHs of most foods are acidic to neutral, not basic. The polyCD did not adsorb hydrophobic

amino acids examined. This selectivity is also advantageous for the removal of BPA from foods. It is concluded that polyCD is found to be an effective adsorbent to remove BPA contaminated in liquid foods.

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