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Removal of Bisphenol A from Aqueous Solutions by Inclusion and Adsorption on Cyclodextrin Immobilized in the Thermosensitive Gel

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Thermosensitive cyclodextrin gels are synthesized to construct an absorbent of water-soluble chemicals such as endocrine disruptors or other toxic materials. The lower critical solution temperature (LCST) of hydroxypropyl cellulose (HPC) was not affected by the presence of hydroxypropyl-β-cyclodextrin (HP-β-CD). Adsorption coefficients calculated from slopes and intercepts of the straight lines for the Freundlich isotherm reveal that affinity of bisphenol A molecules to the gel do not depend on the gel temperature; values of 1/n in the swelling and shrinking states of the gel are obtained to be nearly same. In contrast, the adsorption capacity (K_F) of the HPC/HP-β-CD gel crosslinked by 7 wt% divinyl sulfone depends on temperature. The HPC/HP-β-CD gel can adsorb approximately 99% of bisphenol A in the solution even when high concentrated bisphenol A solution (30 ppm) is treated with the gels (bisphenol A adsorption: 9.5 μmol/g-dry gel).

Key words: thermosensitive gel, cyclodextrin, inclusion, endocrine disruptor, bisphenol A

1. INTRODUCTION

Chemicals slightly dissolved in water occasionally have biological effects; removal of chemicals such as endocrine disruptors or other toxic materials from water is indispensable to keep normal ecosystem. In this paper, a new system for removal of toxic chemicals in water is constructed with a thermosensitive cyclodextrin (CD) gel.

Cyclodextrins are cyclic oligosaccharides which have an unique properties; the central cavity of the CD is lined with skeletal carbons and ethereal oxygens of glucose residues [1,2]. This cavity provides lipophilic space, into which molecule of appropriate size can be included. Since CD complex with suitable molecules forms without covalent bonds, the complex is readily dissociated according to the adsorption equilibrium constant at a certain temperature. Application of CD molecules to solve the environmental problems is already reported using the inclusion properties of CD's [3-5]. On the contrary, a thermosenstive hydrogel, which has a lower critical solution temperature (LCST), has been widely studied to apply a variety of systems such as responsive drug delivery, bioreactors, super-absorbents, and other devices [6-13]. It is expected that the adsorption capacity of the gel due to the CD complex can be controlled by temperature, if CD molecules are immobilized within the thermosenstive gel. There are possible some influences; Dense polymer networks surrounding the immobilized CD cavity may disturb the complex formation between the CD molecule and the target chemical. Furthermore, the microenvironment inside gels becomes hydrophobic as temperature increases above the LCST. This can cause an adsorption increase of the target molecules onto the polymer network due to the hydrophobic interaction. To demonstrate the ability of thermosensitive CD gels as absorbents, the plasticizer, bisphenol A was selected as one of the unexpected chemical, which is occasionally detected in ground water or river water.

To construct the thermosensitive cyclodextrin gel, hydroxypropyl cellulose (HPC) is selected to be the skeleton of gels. Since both HPC and CD derivatives also consists of glucose units, it is considered that both molecules are easily crosslinked by divinyl sulfone (DVS) [14,15].

We synthesize new thermosensitive cyclodextrin gels to develop absorbents for endocrine disruptors or other toxic chemicals. Also, the CD gels will be characterized in respect of thermosensitive properties and bisphenol A adsorption.

2. EXPERIMENTAL

2.1 Materials

HPC (Mw 100,000) was purchased from Aldrich. Hydroxypropyl β-cyclodextrin and DVS were purchased from Acros. All other chemicals were of guaranteed grade or the best commercially available.

2.2 Synthesis of thermosensitive cyclodextrin gel

HPC gel Synthesis of HPC gel was carried out as described in the previous papers [14,16]. HPC was dissolved in pH 12 NaOH solution at 22°C. DVS was added to the solution and then the solution was thoroughly stirred for 30 s. The solution was sandwiched between glass plates separated by a rubber gasket (1.5 mm). The final concentrations of HPC and DVS were 7.5 wt% and 1.3 wt%, respectively. The reaction was allowed to proceed for 24 h at 22°C.

HPC/β-CD gel β-CD (0.1 wt%) was dissolved in the pre-gel solution. The gel sheet (1.5 mm) was prepared in the same way.

HPC/HP-β-CD gel HPC and HP-β-CD were dissolved in pH 12 NaOH solution, for which both of the final concentrations were 3.5 wt%. Hydroxy groups of HPC and HP-β-CD were chemically crosslinked by DVS to form the thermosensitive cyclodextrin gel. Initial

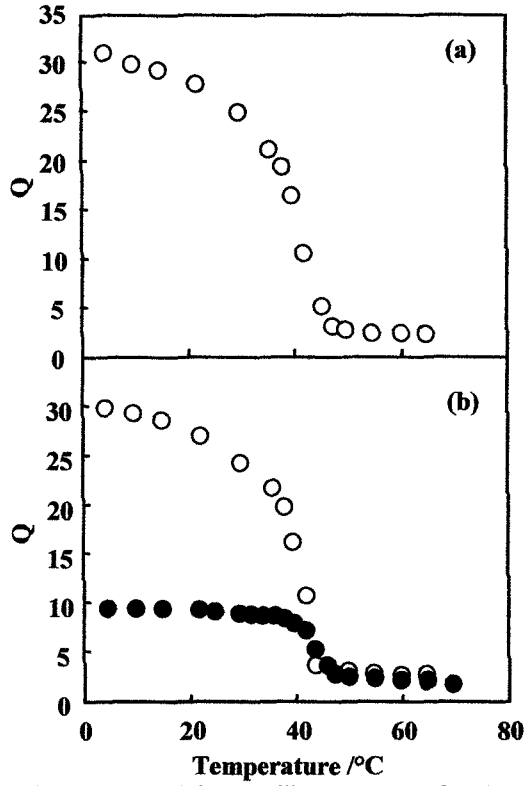

Fig. 1 The equilibrium swelling degree as a function of temperature for the thermosensitive gels. (a) HPC gel (initial HPC concentration: 7.5 wt%) crosslinked by 1.3 wt% DVS. (b) ○: HPC/β-CD gel (initial HPC concentration: 3.5 wt%, initial β-CD concentration: 0.1wt%) crosslinked by 1.3 wt% DVS; ●: HPC/HP- β-CD gel (initial HPC concentration: 3.5 wt%, initial HP- β-CD concentration: 3.5wt%) crosslinked by 5 wt% DVS.

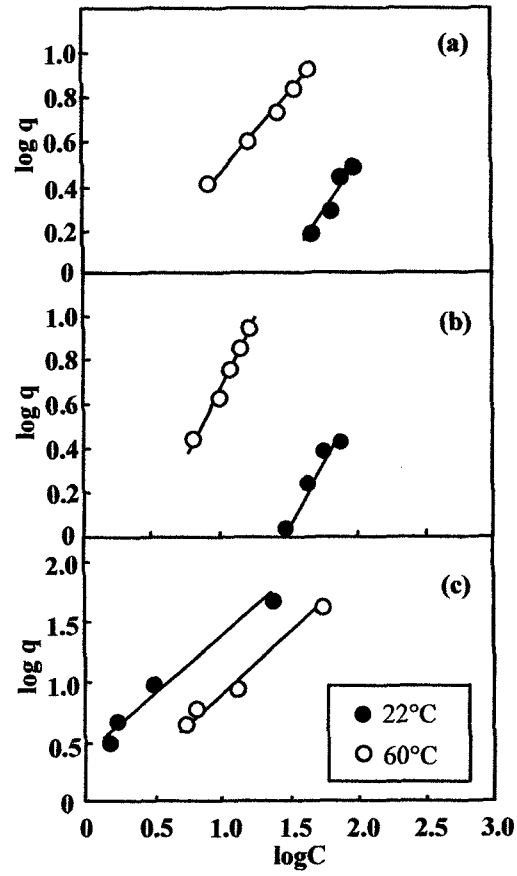

Fig. 2 Freundlich adsorption isotherm of bisphenol A. (a) HPC gel, (b) HPC/β-CD gel (initial β-CD concentration: 0.1 wt%), (c) HPC/HP- β-CD gel (initial HP-β-CD concentration: 3.5 wt%). Initial concentrations of DVS for HPC, HPC/β-CD, HPC/HP- β-CD gels are 1.3, 1.3, and 5.0 wt%, respectively.

concentration of DVS was altered with 3, 5, and 7 wt%.

2.3 Equilibrium swelling degree

The equilibrium swelling degree (Q) at a certain temperature was determined by a gravimetric technique. The equilibrated weight of the gel at a certain temperature (T) was measured after separation from water and blotting the excess water at the gel surface. Then the gel was immersed in water bath at the temperature of T+ΔT. This cycle was repeated from 5 to 70°C. Q was defined as the ratio of the swollen to dry gel weight.

2.4 Adsorption isotherm

Adsorption isotherm tests were conducted as follows. Ten pieces of gel sheets (10×10×1.5mm^3) were immersed in 10 ml of aqueous bisphenol A solution (10, 15, 20, 25, and 30 ppm). The solution was shaken for more than 72 h at 22 or 60°C. Bisphenol A adsorption was determined by absorbance measurements. Data obtained were plotted by the Freundlich equation.

2.5 Adsorption kinetics

Ten pieces of gel sheets (10×10×1.5 mm^3) of HPC gel, HPC/β-CD gel, or , HPC/HP-β-CD gel were immersed in 10 ml of aqueous bisphenol A solution (30 ppm) at 22 or 60°C. Time evolution of bisphenol A adsorption was determined by measurement of the bisphenol A concentration in the surrounding solution. Adsorption ratio was calculated as q_t/q_∞, where q_t and q_∞ are bisphenol A adsorption at time t and at equilibrium, respectively.

3. RESULTS AND DISCUSSION

3.1 Equilibrium swelling degree

HPC gels containing β-CD or HP-β-CD can decrease their weights with increasing temperature (Fig. 1). Since the LCST of HPC gel is reported to be approximately 43.0°C, co-polymerization of CD molecules did not seriously affect the LCST of the gels because HPC and HP-β-CD have the same skeleton consisting of glucose units with the same substituents (hydroxypropyl groups).This result means the microenvironment inside the gels becomes hydrophobic above 43°C.

3.2 Adsorption isotherm

Figure 2 shows Freundlich adsorption isotherm of bisphenol A in HPC gel, HPC/β-CD gel, and HPC/HP-β-CD gel. The relationship between bisphenol

Table I Freundlich isotherm coefficient.

	C_{DVS}	22°C K_f	22°C 1/n	60°C K_f	60°C 1/n
HPC	1.3	0.003	1.59	0.09	1.62
HPC/β-CD*	1.3	0.017	1.24	0.28	1.22
HPC/HP-β-CD*	3	1.4	1.18	1.00	1.03
	5	2.6	0.94	0.87	0.96

*) Contents of β-CD and HP-β-CD respectively were 0.1 and 3.5 wt% just after gel syntheses.

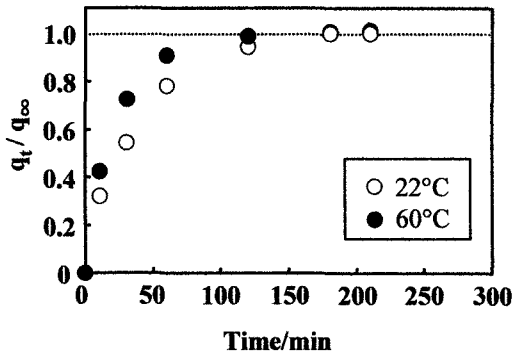

Fig. 3 Time evolution of bisphenol A adsorption onto HPC gels. Ten pieces of HPC gel sheets (10×10×1.5 mm^3 at 22°C) were immersed in 10 ml of 30 ppm bisphenol A solution at 22 or 60°C. The gels were crosslinked by 1.3 wt% DVS.

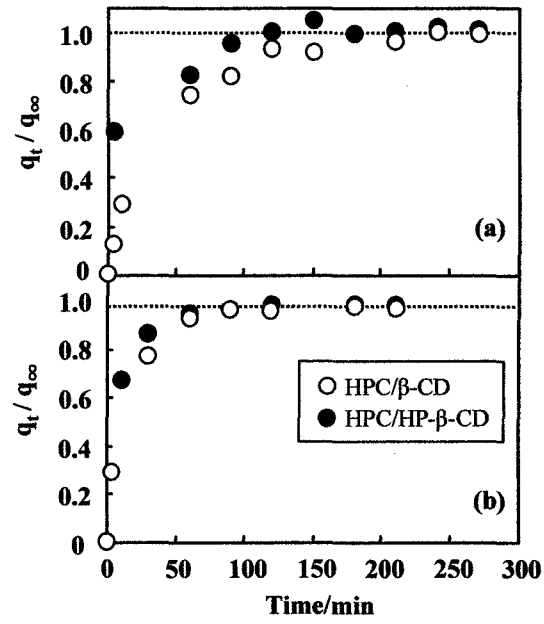

Fig. 4 Time evolution of bisphenol A adsorption onto HPC/β-CD gel and HPC/HP-β-CD gel . Ten pieces of gel sheets (10×10×1.5 mm^3 at 22°C) were immersed in 10 ml of 30 ppm bisphenol A solution at (a) 22 or (b) 60°C . The HPC/β-CD and HPC/HP-β-CD gels respectively were crosslinked by 1.3 and 5.0 wt% DVS.

A adsorption, q (μmol/g-dry gel), and equilibrium concentration of bisphenol A, C (μmol dm^{-3}), is expressed as

$$q = K_f C^{\frac{1}{n}}$$

where K_f and 1/n are the Freundlich parameters, respectively. According to Fig. 2, the plots fell on straight lines irrespective of temperature. The Freundlich parameters obtained are summarized in Table I. Values of 1/n as the affinity parameter between the target molecule and the gel seem not to depend on the temperature. On the contrary, K_f values are quite different; K_f's with and without 0.1 wt% CD at 22°C are obtained to be 0.003-0.017, while these values increase to 0.09-0.28 at the shrinking state of the gels. The possible explanation is that the hydrophobic polymer chains become easy to adsorb bisphenol A molecules containing phenyl groups above the LCST of the gel. In contrast, adsorption capacity of HPC/HP-β-CD gel decreased from 1.4-2.6 to 1.00-0.87 as temperature increased above the LCST. When 3.5 wt% CD molecules are immobilized in the gel, K_f values at 22 or 60°C (0.87 – 2.6) are much larger than those of HPC or HPC/β-CD gel (0.003 – 0.28). Since the CD cavity was surrounded by the polymer aggregation due to hydrophobic interaction at 60°C, the adsorption capacity decreased at the shrinking state of gels.

3.3 Adsorption kinetics

Time dependence of bisphenol A adsorption in the HPC gels is shown in Fig. 3. It took approximately 2 h to equilibrate irrespective of adsorption capacity (K_f =0.003, or 0.09). Figure 4 shows that the adsorption profiles for HPC/β-CD and HPC/HP-β-CD gels. This shows that q_t at 22 and 60°C reached to be equilibrium at around 2 h and adsorption rates do not depend on the temperature.

3.4 Removal of bisphenol A from aqueous solution

Three kinds of gel sheets were immersed in bisphenol

Table II Temperature dependence of bisphenol A removal ratio using thermosensitive cyclodextrin gels.

	p	22°C C_0	22°C C_∞	22°C q_∞	22°C r	60°C C_0	60°C C_∞	60°C q_∞	60°C r
	wt%	ppm	ppm	μmol/g-dry gel	%	ppm	ppm	μmol/g-dry gel	%
HPC	1.3	30	20.3	3.1	32.1	30	3.6	8.5	88.0
HPC/β-CD*	1.3	30	21.8	2.6	27.1	30	3.7	8.4	87.6
HPC/HP-β-CD*	3	30	1.1	9.3	96.3	30	1.3	9.2	95.7
	5	30	0.8	9.4	97.3	30	2.0	9.0	93.3
	7	30	0.4	9.5	98.7	30	15.6	4.6	47.7

*) Contents of β-CD and HP-β-CD respectively were 0.1 and 3.5 wt% just after gel syntheses.

A solutions of 30 ppm (C_0) until the adsorption reached to be equilibrium. The equilibrium concentration of bisphenol A (C_∞), removal ratio of bisphenol A from the solution (r), and q_∞ are listed in Table II. The removal ratio increased from 27-32 to 88%, when the HPC or HPC/β-CD gels is immersed in solutions at 60°C. This is because of the greater hydrophobicity of the gel itself above the LCST. In cases the HPC/HP-β-CD gels are used as absorbents, removal ratio is obtained to be approximately 96-99% even when high concentrated solution (30 ppm) is applied. Since the HPC/ HP-β-CD gel crosslinked by 7 wt% DVS can drastically alter the affinity to bisphenol A, this means the adsorption equilibrium constant can be controlled by the temperature. Consequently, adsorbed bisphenol A molecules on the gel can be reversibly desorbed by the temperature. Further investigation is needed to be clarify the temperature-dependent adsorption/desorption properties of the thermosensitive cyclodextrin gels.

4. CONCLUSION

β-CD or HP-β-CD molecules are immobilized in the thermosensitive HPC gels with the LCST of approximately 43°C. As immobilization of the CD derivatives did not affect the LCST of the HPC gels, the volume of the thermosensitive CD gels can be controlled by temperature. The plots of the Freundlich isotherm for all the examined gel fell on straight lines. The Freundlich coefficients show that the affinity between the gel and the bisphenol A is independent of the temperature; values of 1/n at swelling and shrinking states of the gel are approximately same. However, the adsorption capacity can be controlled by temperature.

HPC/HP-β-CD gels are useful to remove the dissolved bisphenol A in aqueous solution, and bisphenol A of approximately 99% in the solution is separated from the bisphenol A solution of 30 ppm (bisphenol A adsorption: 9.5 μmol/g-dry gel).

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