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Removal of Phthalic Acid Esters from Aqueous Solution by Inclusion and Adsorption on β-Cyclodextrin

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Removal of phthalic acid esters (PAEs) by the formation of inclusion complexes with β-cyclodextrin (β-CD) in aqueous solution was studied. According to the measurements of fluorescence and NMR spectroscopy, it was confirmed that PAEs were included into the β-CD cavity. The stability constants of the β-CDPAE complexes were varied depending on the alkyl chain length of the PAEs. The adsorption isotherms of PAEs and β-CD polymer (β-CDP) were well described by Freundlich isotherm equations, and the adsorption capacity varied according to the stability constant. PAEs were well adsorbed by β-CDP both in batch and in a column system, and the PAEs were also released from β-CDP by shaking with a mixture of methanol and water. The recovery efficiency was varied with the mixture ratio of methanol and water, and the recovered β-CDP was reusable as an adsorbent.

Introduction

Phthalic acid esters (PAEs) are commonly used as plasticizers in various kinds of chemical products such as poly(vinyl chloride) and polyethylene to impart flexibility. As a result of the widespread and abundant use of PAEs, they have been widely dispersed and detected in waters and sediments (*1*). The toxicity or biological effects of PAEs have been reported (*2, 3*); therefore, it is very important to establish a method for removal of PAEs from wastewater and sediments. Some kinds of removal methods for PAEs, such as biodegradation, coagulation, or adsorption, have been reported to date. The bioconversion of PAEs under both aerobic and anaerobic conditions have been investigated (*48*), and their biodegradation by activated sludge has also been demonstrated (*9*). However, those methods required a long time to render the PAEs harmless, and microorganisms could hardly degrade them completely or remove them completely from aqueous solution. Although coagulation including flocculation is useful for the removal of organic micropollutants and its removal mechanism has been reported (*10*), coagulation by ferric chloride was not effective. On the other hand, adsorptive removal by activated carbon and biosorption by bacteria were effective (*11, 12*). Usually the activated carbon used in water treatment is treated by a heat procedure or steam for recovery; therefore, it is difficult to reuse the materials adsorbed on the activated carbon.

In this paper, a unique removal method for PAEs using β-cyclodextrin (β-CD) and its polymer (β-CDP) as an adsorbent has been investigated. Cyclodextrins (CDs) are cyclic oligosaccharides converted from starch, and they and their derivatives have the unique property of forming inclusion complexes with various low-polarity or nonionic organic compounds (*13, 14*). Some papers reporting that CDs and their derivertives were applied for solving the environmental problem have been reported recently such as elution of heavy metals and organic compounds from soil (*15*), solution and destruction of chlorinized carbon (*16*), and extraction of pesticides from soil (*17*). Although few reports of the inclusion formation of β-CD with PAEs have been published, the association between them is easily presumed to form because of their chemical structures. β-CDP is a polymer cross-linked with epichlorohydrin and is known for its adsorption such as drugs (*18*), bitter compounds in food (*19, 20*), cholesterol (*21*), and other chemical compounds (*22, 23*) and is also used as a stationary phase for liquid chromatography (*24*).

β-CD is expected to form inclusion complexes selectively with PAEs not with alkali metals or inorganic compounds. This suggests that β-CDP may be more useful as an adsorbent than activated carbon. The recovery of PAEs from β-CDP and its recycle use have also been studied.

Experimental Section

Materials. Analytical grade dimethyl (DMP), diethyl (DEP), dipropyl (DPP), dibutyl (DBP), diheptyl (DHpP), and di-(2-ethylhexyl) phthalate (DEHP) were purchased from Tokyo Kasei Co., Ltd. β−Cyclodextrin (β-CD) was obtained from Japan Maize Co., Ltd., and was recrystallized twice before use. β-CD polymer (β-CDP), cross-linked β-CD with epichlorohydrin, was a product of the Japan Maize Co., Ltd and was kindly given to us. It was prepared as follows: 100 g of β-CD and 152 g of epichlorohydrin were mixed in 250 mL of distilled water containing 20% of sodium hydroxide at 50 °C. The mixture was added dropwise to the magnetically stirred liquid paraffin (40 °C) and was allowed to stand overnight at the same temperature. The beads were separated from the solution and washed successively with hexane, acetone, and distilled water more than three times. β-CDP was vacuum-dried at 60 for 2 days. It was almost spherical in shape, and the diameter range was about 0.12 mm. The density of β-CDP swelling with water was 1.48 g cm^{-3}. The presumed mole ratio of β-CD/epichlorohydrin from the reaction mixture was 1:1.8, and the presumed mole equivalent of β-CD was 0.37 mmol g^{-1}. β-CDP was rinsed twice in diluted water and methanol separately and vacuum-dried at 60 °C for 2 days before use (*25*). The structure, preparation, and properties of β-CDP have already been described (*26*), and the structures of β-CD and β-CDP are shown in Figure 1.

Inclusion and Stability Constants Measurements. To confirm the association of PAEs with β-CD, nuclear magnetic resonance (NMR) and fluorescence spectra were demonstrated. NMR spectra were obtained at 400 MHz with a JEOL JNM-GSE400 NMR spectrometer. Proton NMR spectra were recorded in D_2O at 25 °C, and the changes in the resonance chemical shifts were measured from β-CD mixed with PAEs. They were compared to those of β-CD only, and chemical shifts (δ) were shown in ppm or Hz relative to the HOD peak. Fluorescence spectra were recorded on a Hitachi Model F-4010 spectrofluorimeter with a narrow emission slit (1 nm) at 25 °C, and the excitation wavelength was 350.0 nm.

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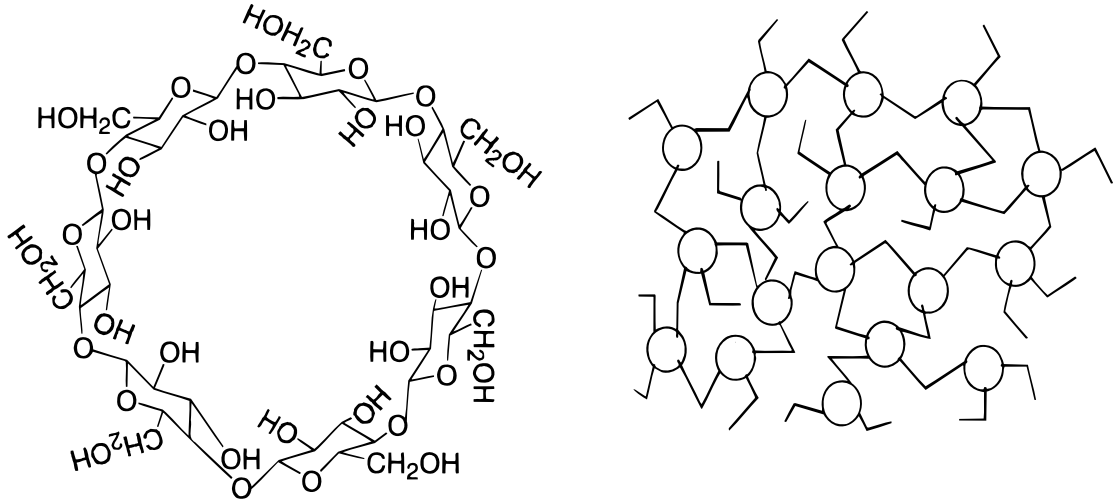

FIGURE 1. Structures of β-CD (1) and β-CDP (2).

Stability constants of PAEs with β-CD were determined with a competitive inhibition method using the fluorescence intensities of 6-(*p*-toluidino)-2-naphthalenesulfonic acid (TNS) on the concentration of PAEs. The concentrations of TNS and β-CD were fixed at 5 μM and 0.2 mM, respectively, and PAEs were changed from 0 to 10 mM to determine the stability constants of PAEs with β-CD. The system is expressed as the following two chemical equilibria:

$$\text{CD} + \text{TNS} \rightarrow \text{CD}\cdot\text{TNS} \quad (1)$$

$$\text{CD} + \text{PAE} \rightarrow \text{CD}\cdot\text{PAE} \quad (2)$$

The initial and equilibrium concentrations were designated by T_0 and T for TNS, P_0 and P for PAE, and C_0 and C for CD, respectively. The association constants (K_0) foe eq 1 and (K) for eq 2 are represented by

$$K_0 = \frac{T_0 - T}{CT} \quad (3)$$

$$K = \frac{P_0 - P}{CP} \quad (4)$$

from eqs 3 and 4, C and $P_0 - P$ are given by

$$C = \frac{T_0 - T}{K_0 T} \quad (5)$$

$$P_0 - P = \frac{K(T_0 - T)P}{K_0 T} \quad (6)$$

From eqs 1, 2, 5, and 6, C_0 is given by

$$C_0 = C + (P_0 - P) + (T_0 - T) \quad (7)$$

$$= \frac{(T_0 - T)(1 + KP + K_0 T)}{K_0 T} \quad (8)$$

Since the value of T is very small as compared with C and P under the experimental condition of $T \ll C \ll P$, would be approximated by P_0, and eq 8 is represented by

$$C_0 = \frac{(T_0 - T)(1 + KP_0)}{K_0[T_0 - (T_0 - T)]} \quad (9)$$

$$T_0 - T = \frac{K_0 T_0 C_0}{1 + KP_0 + K_0 C_0} \quad (10)$$

On the other hand, the observed fluorescence intensity I_0 and I are given by

$$I_0 = i_0 T_0 \quad (11)$$

$$I = i_0 T + i_c(T_0 - T) \quad (12)$$

where i_0 is the mole fluorescence intensity of TNS in water and i_c is the mole fluorescence intensity of TNS in CD solution. Then the deference I from I_0 is given by

$$I - I_0 = (i_c - i_0)(T_0 - T) \quad (13)$$

from eqs 10 and 13

$$I - I_0 = (i_c - i_0)\frac{K_0 T_0 C_0}{1 + KP_0 + K_0 C_0} \quad (14)$$

$$\therefore \frac{K_0 T_0 C_0}{I - I_0} = \frac{1 + K_0 C_0}{i_c - i_0} + \frac{KP_0}{i_c - i_0} \quad (15)$$

The Benesi-Hildbrand equation (*27*) of TNS–β-CD is described as

$$\frac{T}{I - I_0} = \frac{1}{K_0 i_c C} + \frac{1}{i_c} \quad (16)$$

K_0 is easily determined from the intercept and the slope of a plot of $1/(I - I_0)$ vs C in eq 16, and K is also obtained from the intercept and the slope of a plot of $1/(I - I_0)$ vs P_0 in eq 15.

Adsorption Isotherm. Adsorption isotherm tests for PAEs on β-CDP were conducted using 300-mL flasks. One gram of β-CDP and 100 mL of 5 mM phosphate buffer (pH 7.0) added with one of the PAEs and varying the concentration (0–12 mM) were placed in the flasks. They were shaken for 24 h at 25 °C to ensure the system's equilibrium. Samples were analyzed for PAEs by UV spectra measurement or gas chromatography. UV absorbance measurements were performed using a JASCO spectrophotometer Ubest-55, and gas chromatography analysis was performed using an HP gas chromatograph model 5890.

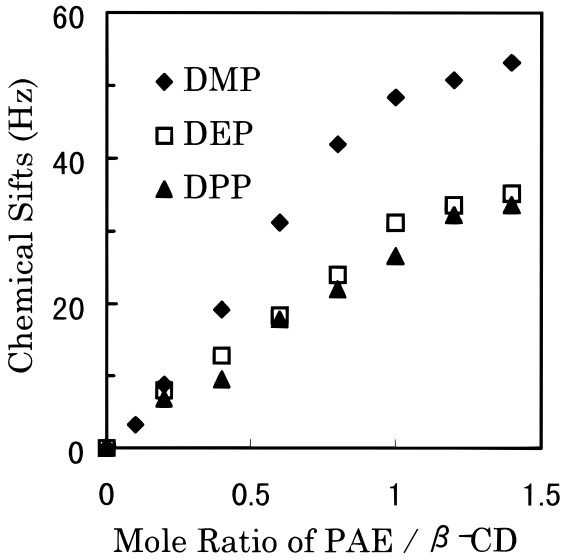

FIGURE 2. Dependence of the H-5 chemical shifts of β-CD on the mole ratio of PAE/β-CD. The spectra were obtained at 400 MHz ^{1}H NMR spectrometer and were recorded in D_2O at 25 °C.

Kinetic Adsorption Tests. Batch mode experiments for adsorption of PAEs on β-CDP at 25 °C were performed in 300-mL flasks with 100 mL of aqueous solutions containing 5 M of each PAE and 1 g of β-CDP. The solutions and β-CDP were placed in flasks and shaken at 100 rpm in a shaker; the residual concentration of the PAEs in the flasks was then monitored at each sampling time. Adsorption tests of each PAE in an aqueous solution containing 1 mM Fe^{2+} and 1 mM Ca^{2+} were also performed according to the same procedures.

Column Tests. The continuous column treatment test was done using a Pyrex tube that was 13 mm in diameter and 300 mm long with a water jacket. Five grams of β-CDP was loaded on the column on a small layer of glass wool. An aqueous solution containing 0.2 mM DMP or DPP was fed at a 1.3 mL min^{-1} rate into the column. The effluent from the column was periodically sampled, and each PAE concentration was determined. The column was maintained at a constant temperature by circulating heated or cooled water in the column jacket, and the tests were performed at 25.0 ± 0.2 °C.

Recovery of the PAEs and Reuse of β-CDP. β-CDP with previously adsorbed PAE was dried at 60 °C and then shaken with a 100-fold volume of solvent mixed with water and methanol in order to recover the PAE. The mixture ratio of methanol and water was varied over the range of 10:0 to 4:6. The β-CDP was washed with water and dried at 60 °C for reuse.

Results and Discussion

Inclusion Complexes. NMR is very useful to prove the formation of inclusion complexes because the protons of both the host and guest would be affected and reflected by chemical shift variation in both species. The NMR spectrum of β-CD (2 mM) consisted of peaks from six kinds of protons (H-1−H-6). The addition of DMP to the β-CD solution caused a remarkable upfield shift of the signals of both the H-3 and H-5 protons of β-CD. The H-5 proton value varied from 3.79 (DMP was free) to 3.67 ppm (DMP was equal to 1 mol of β-CD), and the H-3 proton value varied from 3.90 to 3.81 ppm. Those chemical shifts were saturated in the case where the DMP was added at more than equimolar concentration to β-CD. The chemical shifts of other protons of β-CD were smaller than those of the H-3 and H-5 protons. Figure 2 shows the PAE titration curves of the H-5 proton of β-CD. This observation is the first clue to the formation of an inclusion complex with an equimolar complex because these protons are located inside the hydrophobic β-CD cavity (*28*−*31*). Therefore, it was found that PAEs were included in the β-CD cavity by forming an equimolar complex.

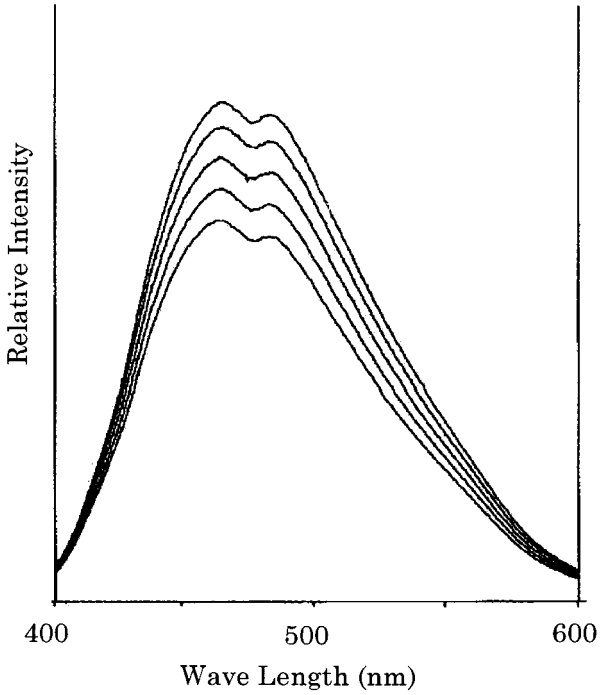

FIGURE 3. Variation of the fluorescence spectra by adding DMP (from top to bottom: 0, 0.5, 1.0, 2.0, and 3.3 mM) to the TNS−β-CD solution.

TABLE 1. Stability Constants between β-CD and PAEs

PAE	K^a	log K_{ow} [b]
DMP	82 ± 2.1	1.60
DEP	107 ± 8.9	2.42
DPP	300 ± 26	3.31[c]
DBP	1160 ± 211	4.50
DHpP	2142 ± 178	6.95[c]
DEHP	928 ± 91	7.54

[a] K values were calculated by a plot of eq 15 with the standard deviation at the 95% confidence level. [b] Listed from ref *32*. [c] This value was estimated by the HPLC method in ref *33*.

The addition of PAEs to the TNS−β-CD solution decreased the fluorescence intensity. Figure 3 shows the decrease of the fluorescence intensity in the case of adding DMP (0, 0.5, 1.0, 2.0, and 3.3 mM) to the TNS−β-CD solution. This observation suggests that TNS was dissociated from β-CD by the presence of PAEs, and the PAEs seemed to form complexes with β-CD instead of TNS. This method has been demonstrated for many chemical products (*31*), but few applications for PAEs have ever been reported. The stability constant (K) of each PAE with β-CD could be calculated by the relationship between the PAE concentrations and the alterations in fluorescence intensity using eq 15. The K_0 obtained by eq 16 was 220 M^{-1}. The calculated stability constants of the β-CD−PAE complexes increased with increasing alkyl chain length of the PAEs except for DEHP as in Table 1. Although the correlation coefficient between the concentration of PAE and the difference of the fluorescence intensity were 0.988 for DHxP and 0.987 for DEHP, K of DHpP and DEHP in Table 1 should be treated only as the tentative values because DHpP and DEHP were added excessively over the range of the solubility to calculate it. It is considered that PAE with a longer alkyl group could form a more stable complex than

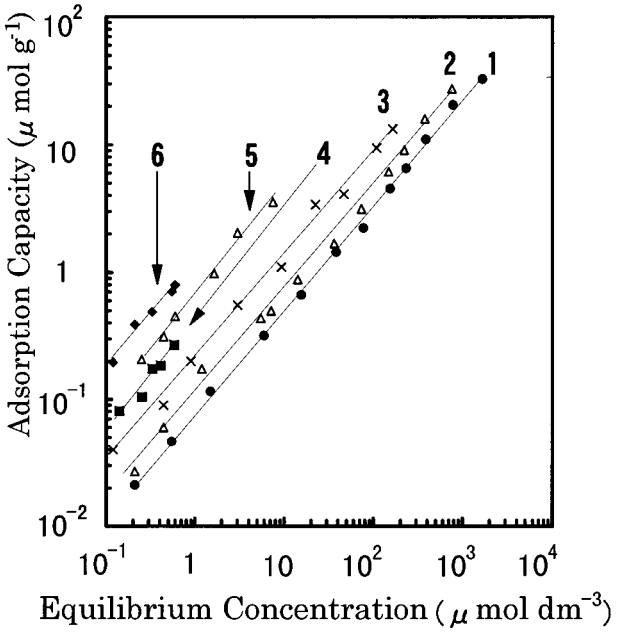

FIGURE 4. Freundlich adsorption isotherms of PAEs at 25 °C. (1) DMP, (2) DEP, (3) DPP, (4) DEHP, (5) DBP, and (6) DHpP.

that that with a short alkyl group because it tended to be more hydrophobic than that having a short alkyl chain. The octanol−water partition coefficients (K_{ow}) of PAEs are also shown in Table 1. The values of K_{ow} were provided by the refs 32 and 33, and the values of DPP and DHpP were estimated by the HPLC method (*33*). Although the relationship between log K_{ow} and K about DMP, DEP, DPP, and DBP represented good correlation (log K_{ow} = 1.01 log K − 2.58, r = 0.964), others did not express such good correlation. That might depend on the experimental condition or K that is not necessarily proportional to the hydrophobicity of a guest. The fact that the stability constant of DEHP is smaller than that of DBP despite a more hydrophobic property could be considered due to the steric hindrance between the ethyl side chain of DEHP and the β-CD cavity contributing to the weakening of the linkage between them.

Adsorption Isotherm. Graphic presentations of the adsorption isotherm results are given in Figure 4, and the data have been plotted according to the Freundlich isotherm. The adsorption capacity appeared to remarkably increase with increasing equilibrium concentration, and the relationship between the adsorption capacity and the equilibrium concentration could be described with the Freundlich equation described according to

$$q = K_f C^{1/n} \quad (17)$$

where q is the adsorption capacity (μmol g^{-1}) and C is the equilibrium concentration (μM). By plotting log q as the Y axis and log C as the X axis, K_f and $1/n$ were calculated as Freundlich parameters, and the results and the correlation coefficients are listed in Table 2. The isotherm for activated carbon was also described by Freundlich equation, and the isotherm for aluminum flock was described by BET equation (*10, 11*). The coefficients K_f and $1/n$ of the Freundlich equation ($q = K_f C^{1/n}$) in the ref 11 are 27 and 0.42 for DMP, 600 and 1.01 for DBP, and 7.3 and 0.76 for DEHP, where q is the adsorption capacity (mg g^{-1}) and C is the equilibrium concentration (mg L^{-1}). The coefficients are different from the kind of PAE in the case of β-CDP. According to Figure 4, the isotherms of DMP and DEP were linear with almost 4 orders of magnitude in each equilibrium concentration. Otherwise, DBP, DHpP, and DEHP were linear within less than 2 orders of magnitude in each PAE equilibrium concentration because of their lower solubility than DMP or DEP. Each isotherm had a value near $1/n$, indicating that each curve had a similar shape as in Figure 4 and Table 2. On the other hand, the K_f values were quite different, and this means that the adsorption capacity was quite different with each PAE. The magnitude of the adsorption capacity was correlated with the PAE stability constant. Thus, the adsorption of PAE on a β-CDP is considered to be caused by the inclusion of PAE in β-CD.

TABLE 2. Freundlich Isotherm Coefficient in Eq 17[a]

PAE	K_f	$1/n$	r
DMP	0.075	0.82	0.997
DEP	0.109	0.82	0.998
DPP	0.208	0.81	0.997
DBP	0.683	0.85	0.994
DHpP	1.21	0.82	0.975
DEHP	0.413	0.86	0.954

[a] The isotherm coefficients were measured at 25 °C, and r is the correlation coefficient between the adsorption capacity (q) and PAE concentration (C) in eq 17.

TABLE 3. Adsorbed Ratio (%) of PAEs on β-CDP in the Batch Test[a]

	solution A shaking time (h)				solution B shaking time (h)	
PAE	0.5	1	2	5	2	5
DMP	21.9	25.0	27.3	28.1	26.5	27.4
DEP	30.8	33.3	35.9	38.5	37.2	39.6
DPP	55.6	61.1	63.6	64.1	62.8	63.4
DBP	71.9	78.4	83.8	87.5	83.0	88.6
DHpP	36.2	51.1	71.0	88.1	72.5	86.8
DEHP	30.5	45.3	65.2	84.6	63.4	85.7
Fe					−2.1	0.6
Ca					−2.0	−1.6

[a] Each solution, 100 mL of aqueous solutions containing 5 μM of each PAE and 1 g of β-CDP, was shaken at 25 °C and 100 rpm. Solution B was contained 1 mM Fe^{2+} and 1 mM of Ca^{2+}.

Kinetic Adsorption Tests. Table 3 (solution A) presents the adsorbed ratio (%) of each PAE in the flask with shaking time of 0.5, 1, 2 and 5 h. The order of the adsorbed ratio was in accord with the value of the stability constant of each PAE. This suggests that the adsorption efficiency of PAE significantly depended on the inclusion complex forming between PAE and β-CD. To investigate the influence of metal ions, a solution containing 1 mM Fe^{2+} and 1 mM Ca^{2+} was used for a batch adsorption test. The diluted water was degassed by bubbling in helium gas, adjusted to pH 3.0 with phosphate buffer after adding 1 mM Fe^{2+} and 1 mM Ca^{2+}, and was degassed with helium gas again. In the case of using a solution containing 1 mM ions, the adsorption efficiency of each PAE was not affected by the ions, and the ions were not adsorbed on the β-CDP as in Table 3 (solution B). This suggests that the β-CDP adsorbed only PAE and could be advantageously reused.

DPP, DEP, and DMP were not so well removed by a batch adsorption treatment because of their smaller stability constants. Therefore, multistage separation tests with them were carried out to increase the removal efficiency. A multistage separation mode was performed using a repeated batch adsorption technique. The tests were conducted using 300-mL flasks in which were placed 100 mL of aqueous solution containing 0.2 mM DMP, DEP, or DPP and 1 g of β-CDP. After 30 min of shaking, the solutions were filtered with glass microfiber filters and placed in other 300-mL flasks. New β-CDP was added at 1% based on the weight of the

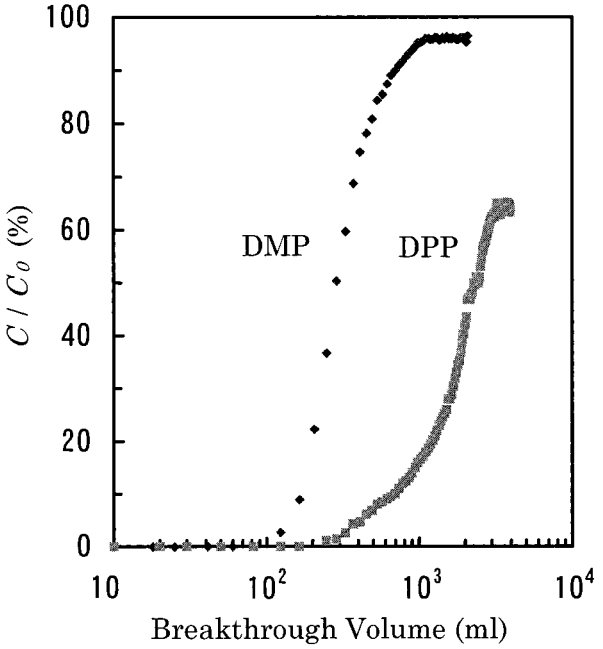

FIGURE 5. Breakthrough curves of β-CDP for DMP and DPP at 25 °C C and C_0 are the effluent and influent concentrations of PAE. 5 g of β-CDP was loaded on the column, and the influent PAE concentration was 0.2 mM.

TABLE 4. Breakthrough Volume of β-CDP for DMP and DPP[a]

	phthalate					
	DMP			DPP		
effluent/influent (C/C_0)	0.05	0.1	0.2	0.05	0.1	0.2
volume (mL)	137	168	202	370	680	1220
breakthrough capacity (μmol g^{-1})	5.45	6.62	7.70	15.2	26.6	45.2

[a] The influent concentration of each PAE was 0.2 mM, and the aqueous solution was fed at 1.3 mL min^{-1} to the column that was loaded with 5 g of β-CDP. The pore volume, the linear velocity, and the residence time were 26.5 cm^3, 0.98 cm min^{-1}, and 20.4 min, respectively.

solutions, and the samples were shaken for 30 min, filtered, and placed into other 300-mL flasks again. After four repetitions of the procedures with a shaking time of 2 h, the removal ratios of PAEs (= removed PAE/initial PAE) were significantly raised, such as 66.9% DMP, 69.2% DEP, and 88.6% DPP. The removal ratio was improved by about 1.4−2.5 times as compared with the single batch test with the same shaking time.

Column Adsorption Test. PAE removal experiments using a column were performed at 25 °C. Figure 5 illustrates the breakthrough curves, and Table 4 demonstrates the breakthrough capacity (*34*) for β-CDP. The pore volume was almost 26.5 cm^3, then the linear velocity and the residence time were 0.98 cm min^{-1} and 20.4 min, respectively. The data show that a larger amount of DPP was adsorbed on β-CDP as compared to DMP and the breakthrough capacity ratio of DMP/DPP was in the range of 0.17−0.37 in which C/C_0 was 0.05−0.2. C/C_0 of DMP easily came close to 95% because the adsorption capacity of DMP was very small. On the other hand, because of the large adsorption capacity of DPP, a larger amount of breakthrough volume as compared with DMP was obtained. C/C_0 of DPP increased gradually until 3000 mL of the breakthrough volume, and the change of C/C_0 of DPP became smaller over 3000 mL of the effluent. The difference in the breakthrough capacity could be interpreted to be due to the stability constant of DMP being smaller than that of DPP, and the adsorption is probably provided by the inclusion of the PAEs in the β-CD cavity. This suggests that a compound having a small stability constant such as DMP should be treated over a long contact time with β-CDP by a large column volume or a proper flow rate.

TABLE 5. Recovery Ratio of PAE from β-CDP with Methanol Aqueous Solution[a]

methanol−water ratio	recovery ratio (%)	
	DMP	DPP
10:0	71.8	68.4
9:1	83.6	79.6
8:2	92.5	91.7
7:3	88.5	85.1
6:4	84.0	77.6
5:5	76.4	68.3
4:6	65.7	61.1

[a] β-CDP, with previously adsorbed DMP or DPP, was shaken for 2 h with 100 times its weight of methanol−water solution.

TABLE 6. DPP Adsorption Rate of β-CDP on Repeated Runs[a]

repetition times	adsorption rate (%)
0	63.6
5	61.5
10	60.8
20	59.4

[a] The test was repeated as the cycle of adsorption of DPP on β-CDP in aqueous solution and the release from β-CDP using 80% of methanol solution. The adsorption rate of β-CDP was tested after the cyclic tests had been performed.

Recovery of PAEs and Recycling of β-CDP. A practical method of both recovering PAEs and recycling β-CDP was performed with a mixture of methanol and water. One gram of β-CDP, with some previously adsorbed amount of PAE, was shaken for 2 h with 100 mL of solvent using aqueous methanol. The mixture ratio of the solvent was varied from 100 to 40% of methanol, and the recovery ratio for each solvent was calculated based on the ratio of the recovered PAE amount relative to the PAE amount previously adsorbed on β-CDP. The recovery efficiency depended on the methanol/water ratio, and the most efficient mixing ratio of the solvent was 80% methanol as in Table 5. PAE tended not to be released from β-CDP in the methanol-rich solvent although PAE could be dissolved into such solvent. It appears that the balance between the tendency of PAE adsorption on β-CDP and PAE dissolubility into the solvent is important. It is considered that β-CD would be restricted of the free molecular motion in alcohol because it hardly dissolves in the solvent. Consequently, previously included PAE could hardly be released from β-CD in alcohol-rich solvent although PAE is much more soluble in alcohol than in water. β-CD tends to dissolve and could be free on the molecular motion in the solvent containing 20% of water; the more water would be increased, the more the binding force between β-CD and PAE would become stronger and PAE could not release from β-CD.

Because the β-CDP that released DPP had almost equal adsorption capacity relative to the initial value, the recycle use of β-CDP was repeated 20 times by cycling the adsorption and releasing of DPP. The solvent for the adsorption test was a 0.2 mM DPP aqueous solution, and that for the release test was a solution of 80% methanol and 20% distilled water. One gram of β-CDP and 100 mL of the solvents were used for the recycling test. Even after 20 cycles of the recycling tests were performed, more than 90% of the adsorption ratio as compared with the initial value was assessed as in Table

6. Thus, the repeated cycling of β-CDP should be predictable based on the recycling test.

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