Preparation of crosslinked β-cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater

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Abstract

BACKGROUND: Phenols are commonly encountered in aqueous effluents from various manufacturing processes such as oil refineries, coke plants, and phenolic resin plants, and are toxic substances that should be removed from the aquatic environment. We describe the preparation of beaded crosslinked β-CyD polymers, and the removal of phenol from raw industrial wastewater discarded from phenolic resin processing by the obtained β-CyD adsorbent.

RESULTS: The crosslinked β-CyD prepolymer was synthesized by treatment of β-CyD with hexamethylene diisocyanate (HDI) at a molar ratio of 1:8. The suspension of the resulting powdery prepolymer in aqueous sodium alginate was added dropwise into an aqueous calcium chloride solution to precipitate the spherical β-CyD prepolymer gels. The spherical prepolymer gel was lyophilized and re-crosslinked with HDI to afford the β-CyD polymer beads. The physical properties of the beads were as follows: average diameter: 3.4 mm; average compressive strength: 2.17 M Pa; porosity: 47.0 %; specific surface area: 3.48 m^2/g. The removal of phenol from raw industrial phenolic wastewater with the β-CyD polymer beads was carried out in either a shaker or upflow column at 25°C. After seven times of accumulated adsorption, the phenol concentration of 89000 ppm decreased to as low as 350 ppm in the former and 490 ppm in the latter.

CONCLUSION: Adsorbent [β-CyD/HDI(1/8)]/HDI polymer beads having a good regular shape and high mechanical stabilities were newly prepared by a stepwise crosslinked method. The results of sorption experiments show that the beads exhibit high sorption capacities toward phenolics in raw industrial wastewater.

Keywords: β-cyclodextrin; phenol removal; polymer beads; diisocyanate network polymer; raw industrial wastewater

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INTRODUCTION

Phenols (phenol and phenolic compounds) are commonly encountered in aqueous effluents from various manufacturing processes such as oil refineries, coke plants, and phenolic resin plants, and are toxic substances that should be removed from the aquatic environment. In our research in a recent article,[1, 2] we carried out an attempt to find a novel cyclodextrin (CyD) polymer for the removal of phenols from raw industrial wastewater discarded from phenolic resin processing, and found that the most efficient removal method was by pulverized crosslinked β-CyD with hexamethylene diisocyanate (HDI) in a 1:8 molar ratio, or pulverized crosslinked Mix-CyD (α-CyD: β-CyD: γ-CyD: dextrin = 30 : 10 : 10 : 50 wt/wt) with HDI, also in a 1:8 molar ratio, with a mean diameter of below 53 μm. However, the types of equipment that can be employed for the removal of pollutants from water are the stirred-tank, fluidized bed, and column. Therefore, the use of adsorbents of large-particle size is advantageous in that the adsorbents can be easily separated from the medium for the purpose of recycling or controlling the removal progress. In this paper, we describe the preparation of beaded crosslinked β-CyD polymers using a stepwise crosslinked method, and the removal of phenol from raw industrial wastewater discarded from phenolic resin processing by the obtained β-CyD adsorbent.

MATERIALS AND METHODS

Experimental apparatus and procedures

Reagents

β-CyD was kindly supplied by Mercian Co., Ltd. (Tokyo) and used without further purification. Sodium alginate (Na Alg.) was purchased from Sigma-Aldrich Japan (Tokyo). Hexamethylene diisocyanate (HDI), dibutyltin dilaurate (BTL), and *N*,*N*-dimethylformamide (DMF) were purchased from Tokyo Kasei Kogyo (Tokyo), and HDI, DMF and benzene were purified by distillation. All other organic and inorganic reagents were of the purest grade and available from commercial sources.

Preparation of spherical porous crosslinked β-CyD polymers

The spherical crosslinked β-CyD polymers were prepared. The methods are the same; only pre-polymer differs, as described in Chart 1. β-CyD prepolymers of low and high crosslinkage were synthesized by treatment of β-CyD with HDI at a molar ratio of 1:2 and 1:8 (mol/mol), respectively.[1, 2] Pasty prepolymers were obtained by the former protocol, and the number-average molecular weight and degree of polymerization were determined to be about 1.12 $\times 10^4$ and 9.6 by mass spectrometry, using a MALDI-TOF/MS Voyager-DE™ PRO (Applied Biosystems Japan, Tokyo). On the other hand, powdery prepolymers were obtained by the latter protocol. Solid prepolymers were ground by ball-milling to give fine particles with a mean diameter of below 53 μm, as previously described.[1, 2]

The suspension of either prepolymers in 1 wt% of aqueous Na Alg. solution (50 - 60 wt%) was added dropwise into an aqueous calcium chloride solution (3 wt%) to precipitate the spherical crosslinked β-CyD prepolymers. Then, the resulting spherical prepolymers were followed by lyophilization (used freezer at -20°C), re-crosslinked with HDI (Prepolymers/HDI = 1/1.5 (wt/wt)) in benzene for 24 h at 80°C, and washed with chloroform and methanol (MeOH). After drying at 60°C *in vacuo,* the crosslinked β-CyD polymers were used as a sorbent for the removal of phenol.

The β-CyD contents of the prepared sorbents were estimated by elemental composition, determined by a CHN elemental analyzer 2400 II (Perkin Elmer Japan

Co. Ltd., Yokohama). The compressive strength area, the specific surface area, and the porous volume of the adsorbents were determined by the use of a tensile and compressive testing machine, STA-1150 (A&D Co. Ltd., Tokyo), a BET[3] apparatus NOVA-1200 (Yuasa-Ionics Co. Ltd., Osaka), and a Pore Master 60-GT (Yuasa-Ionics Co. Ltd.), respectively. The surface properties of the adsorbents were studied by scanning electron microscopy (SEM) with a FE-SEM S-4300 (Hitachi High-Technologies Co., Tokyo) using an accelerating voltage of 3 keV after coating with Pt, as well as optical microscopy with a digital microscope, VH-8000 (Keyence Co., Osaka).

Adsorption Experiments

Equilibrium adsorbent batchwise tests were carried out by placing weighed quantities of the porous β-CyD beads (1.0 g) and samples of phenol wastewater solution (5 cm^3) in a 50-cm^3 Erlenmeyer flask sealed by polyethylene film and shaking the flask for a fixed time in a 25°C chamber at 80 rpm. Aqueous industrial wastewater discharged from phenolic resin processing from Meiwa Plastic Industries, Ltd. (Ube), of which the components were phenol (8.9 wt%), *m*- and *p*- cresols (0.33 wt%), xylenols (0.044 wt%), methanol (9.95 wt%) at pH = 3.0, was used in all adsorption experiments. At arbitrary intervals, aliquots (0.1 - 0.2 cm^3) were withdrawn from the solution, and the concentration of phenol was determined with a capillary gas chromatograph fitted with a flame ionization detector (model GC-6APTF; Shimadzu, Kyoto) employing a Silicone-OV-17/Chromosorb WAW DMCS column (GL Science Inc., Tokyo). The lower limit of the detection was 0.005 wt%.

Adsorption tests with experimental apparatus consisting of a continuous upflow column with a volume of 115 cm^3 (ID 35 mm; height 120 mm) were also carried out (Fig. 1). Twenty-five grams of adsorbent beads were charged, then 125 cm^3 of phenol wastewater solution was supplied to the column and circulated at different liquid velocities for four days. The time-courses of the phenol uptake within 4 days were followed by determination of the concentration of phenol, as well as in the case of the batchwise experiment. All experiments were conducted at 25°C.

RESULTS AND DISCUSSION

Preparation of β-CyD polymer beads

The β-CyD polymer beads thus prepared are designated hereafter as β-CyD/HDI(*n*)]/HDI, where *n* refers to the molar ratio of HDI to β-CyD in the preparation of the prepolymer.

Table 1 summarizes the physical properties of the adsorbent beads. Adsorbents spherical in shape were observed under a microscope (Fig. 2). The scanning electron microscope (SEM) pictures of transverse- and surface-angles for [β-CyD/HDI(1/8)]/HDI beads are shown in Fig. 3.

Preliminary experiments on the performance of β-CyD polymer beads

The capacity of each β-CyD polymer bead was determined by its removal efficiency per 1 gram of beads for the uptake of phenol from 5 cm^3 of wastewater solution for 2 h in the batchwise case. The results in Table 2 show that the phenol removal efficiency of the polymer beads, [β-CyD/HDI(1/8)]/HDI, was not as good as fine polymer powder, β-CyD/HDI(1/8), i.e., prepolymer powder. The beads, however, have higher compressive strength and porosity, and a more regular shape with a diameter of about 3 mm, which is most suitable for industrial purposes (Table 1 and

Fig. 2). Recent developments in the preparation of adsorbents containing polysaccharides such as CyD and their advantages for the removal of pollutants from wastewater were fully reviewed by Crini.[4]

The molar ratio of the adsorbed phenol into the β-CyD moiety in the β-CyD polymer beads was expected to be one or at most two, if the sorption mechanism was solely due to the formation of an inclusion complex between the CyD moiety in the beads and the phenol through host-guest interactions. However, the adsorption behavior of the [β-CyD/HDI(1/2)]/HDI and [β-CyD/HDI(1/8)]/HDI cannot be completely described by this mechanism because the molar ratios of the adsorbed phenol onto the β-CyD polymer beads were 5.5 and 9.5, respectively (Tables 1 and 2). Thus, physical adsorption in the β-CyD polymer network and chemical interactions via the hydrogen bonding formed with phenol between hydroxyl and/or amide groups were also involved in the present sorption process, as described by Crini and Morcellet.[5, 6] The image for the adsorbed phenol onto the β-CyD polymer beads by different interactions was illustrated in Fig. 4.

From the β-CyD residue contents in the polymer beads (in Table 1) and the adsorption results (in Table 2), the phenol sorption capacities for [β-CyD/HDI(1/2)]/HDI, [β-CyD/HDI(1/8)]/HDI, and β-CyD/HDI(1/8) were determined to be 2.79 mmol(g-resin)$^{-1}$, 3.03 mmol(g-resin)$^{-1}$ and 3.74 mmol(g-resin)$^{-1}$, respectively. The phenol sorption capacity of 43.4 μmol(g-resin)$^{-1}$ or 0.1 mmol(g-resin)$^{-1}$ for the β-CyD epichlorohydrin crosslinked network polymers have been reported.[7, 8] Thus, this indicates that the present β-CyD polymer beads remove phenol more effectively than the other β-CyD network polymers. The [β-CyD/HDI(1/8)]/HDI beads showed higher adsorption capacities for phenol than for [β-CyD/HDI(1/2)]/HDI beads, suggesting that the former sobent has a richer polymer network structure suitable for the sorption process. Regardless of bead size, the adsorption capacities of the [β-CyD/HDI(1/8)]/HDI beads were comparable to those of the β-CyD/HDI(1/8) polymer powder. Thus, the polymer beads, [β-CyD/HDI(1/8)]/HDI, were selected as the practical adsorbent beads and solely used in the subsequent experiments.

Performance of β-CyD polymer beads in batchwise adsorption

The time-courses of the phenol uptake with 48 [β-CyD/HDI(1/8)]/HDI polymer beads (1.0 g) were followed during 6 h and 4 days (Fig. 5). As can be seen, 53 % of the phenol was removed within 30 min and 78 % of the phenol was removed at equilibrium after 3 days. With the present [β-CyD/HDI(1/8)]/HDI polymer beads, a two-stage uptake of phenol was observed, while with β-CyD/HDI(1/8) polymer powder only almost instantaneous adsorption reaching equilibrium was observed.[1, 2] This behavior seems to be due to both the increase in particle size and the two-layer structures of the polymer beads resulting from the two stages of crosslinking of β-CyD, as shown in Fig. 3 (A): a hard skin layer (outer layer) of poor permeability and a soft core layer (inner layer) of good permeability.

Next, the removal of phenol with [β-CyD/HDI(1/8)]/HDI beads in the batchwise case was repeated seven additional times with a resulting supernatant solution (Fig. 6). After seven times of accumulated treatment, the concentration of 8.9 wt% phenol decreased to as low as 350 ppm from 89000 ppm.

Regeneration of the β-CyD polymer beads

Regeneration of the [β-CyD/HDI(1/8)]/HDI sorbent was examined following the method of our previous paper.[1, 2] The adsorbed phenols were removed from the adsorbent conducted by soaking it in 50cm^3 of methanol at 25 °C. After 24 h the adsorbent was filtered off and dried *in vacuo*. The results for the removal of phenol using the regenerated β-CyD beads are summarized in Fig. 7. The adsorbent retained about 96% of its original phenol uptake ability even after using it five times because the elution of the phenol included in the polymer beads with methanol was easily accomplished quantitatively under mild conditions.

Mechanical stability of the β-CyD polymer beads in batchwise adsorption

Visual judgment of the breakup was done for all of the 1205 adsorbent beads (25 g), classifying them into three categories-- i.e., unchanged, cracked, and broken (split up into some particles). Each batchwise adsorption was carried out by placing all of the regenerated adsorbents (25 g) and fresh phenol wastewater solution (125 cm^3), in a 300-cm^3 Erlenmeyer flask, and shaking the mix at 80 rpm for 1 day at 25°C. After regeneration, the weight of the beads that belonged to each category was measured to evaluate the mechanical stability of the adsorbent beads. The experimental results are summarized in Fig. 8. During a 10-day period, only 0.9 wt% of the beads had cracked. Hence, β-CyD polymer beads with good physical stability are recommended for practical application of this adsorbent for the removal of phenols from raw industrial wastewater.

Performance of β-CyD polymer beads in an upflow column

One thousand two hundred and five β-CyD polymer beads (25 g) were placed in the column, then 125 cm^3 of phenol wastewater was supplied and circulated at a flow rate of 2.2 - 19.0 cm^3/s in order to permit full fluidization of the adsorbent beads. Fig. 9 shows the effects of the phenol wastewater circulation rate on the phenol removal efficiencies in the upflow column and time plots of the batchwise phenol removal. During the enrichment period of soaking phenol for up to 6 h, the phenol removal efficiencies were greatly affected by the flow rate, and reached equilibrium efficiency after 4 days. These results indicate that adsorption with the β-CyD polymer beads was affected by intra-particle mass transfer limitation, which did not exist in the process with the previous fine β-CyD polymer powder,[1, 2] due to the increase in particle size, the higher density, and/or the lower porosity of the bulk material.

Finally, the removal of phenol with the β-CyD polymer beads in the upflow column was repeated seven additional times with the supernatant wastewater solution (Fig. 10). The adsorbent removed the phenol from acidic/phenolic wastewater containing 89000 ppm phenol to a concentration as low as 490 ppm, after seven times of accumulated treatment.

CONCLUSION

Adsorbent [β-CyD/HDI(1/8)]/HDI polymer beads having a good regular shape with a diameter of 3 mm and high mechanical stabilities for the removal of phenols from phenolic industrial wastewater were successfully prepared by a stepwise crosslinked method. The uptake of phenols from phenolic wastewater with the beads attaining equilibrium fairly slowly due to intra-particle mass transfer limitation was in contrast to the case with the fine β-CyD polymer powder. However, the adsorption employing the present β-CyD polymer beads was easy to operate and could be achieved by various apparatus such as a stirred-tank, packed bed, or fluidized bed (expanded bed).

ACKNOWLEDGEMENTS

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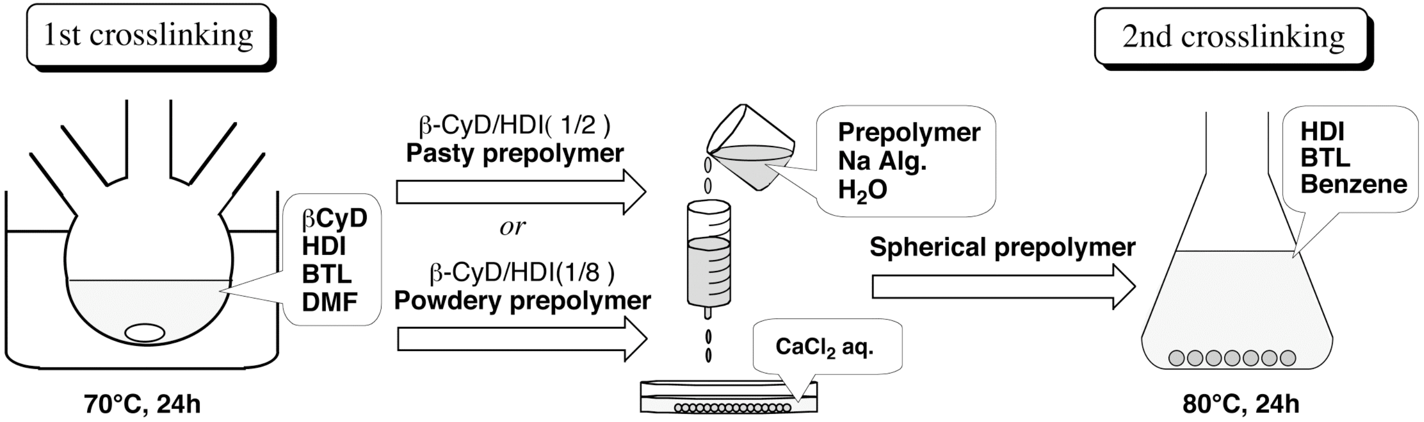
1st crosslinking
βCyD
HDI
BTL
DMF
70°C, 24h
β-CyD/HDI(1/2)
Pasty prepolymer
or
β-CyD/HDI(1/8)
Powdery prepolymer
Prepolymer
Na Alg.
H2O
CaCl2 aq.
Spherical prepolymer
2nd crosslinking
HDI
BTL
Benzene
80°C, 24h

Chart 1

Table 1. Physical properties of the β-CyD polymer beads

Adsorbent	Average diameter (mm)	Bulk density[a] (g/cm^3)	Porosity[a] (%)	Specific surface area[b] (m^2/g)	Compressive strength[c] (M Pa)	β-CyD[d] (μmol/g)
[β-CyD/HDI(1/2)]/HDI	2.7	0.76	44.2	0.75	0.98	507
[β-CyD/HDI(1/8)]/HDI	3.4	0.74	47.0	3.48	2.17	319

[a] Determined by Pore Master 60-GT.

[b] Determined by NOVA-1200.

[c] Determined by STA-1150.

[d] The content of β-CyD residue in polymer beads determined by CHN elemental analyzer 2400 II.

Table 2. The performance of β-CyD polymer beads for phenol adsorption [a, b]

Adsorbent	Separation efficiency [c] %	Residual conc. of phenol wt%
[β-CyD/HDI(1/2)]/HDI [d]	59	3.6
[β-CyD/HDI(1/8)]/HDI [e]	64	3.2
β-CyD/HDI(1/8) [f]	79	1.9

[a] Initial concentration of phenol was 8.90 wt%.

[b] The adsorption was carried out by placing an adsorbent (1.0 g) and a wastewater solution (5 cm^3) in a 50-cm^3 Erlenmeyer flask and shaking the flask in a 25°C chamber at 80 rpm for 2 h.

[c] Separation efficiency (%) was calculated from the difference between the concentrations of phenol before and after adsorption.

[d] Polymer beads (average diameter of 2.7 mm).

[e] Polymer beads (average diameter of 3.4 mm).

[f] Polymer powders (diameter of below 53 μm).

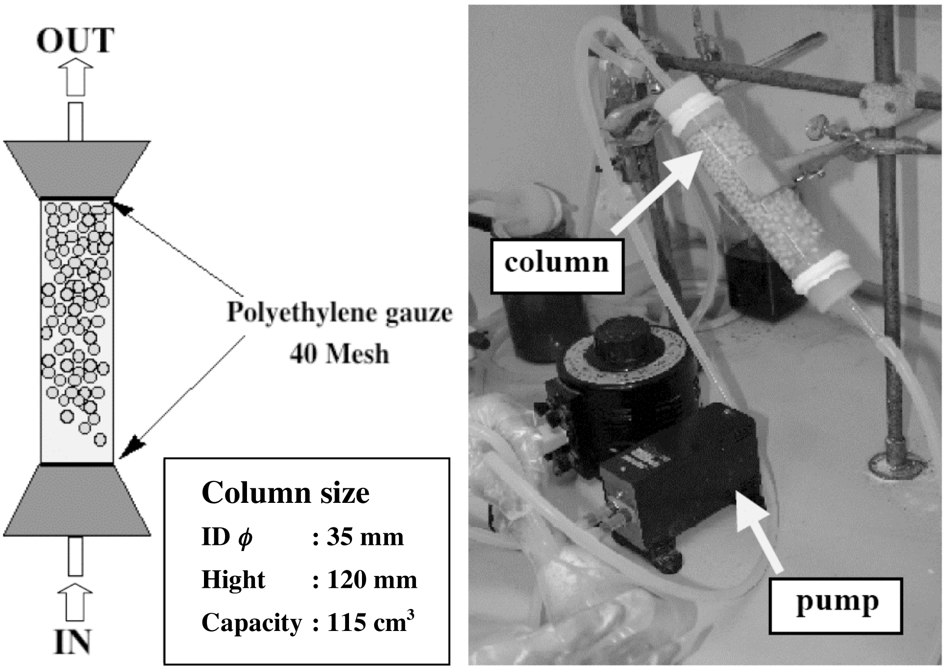

Figure 1. The experimental continuous apparatus.

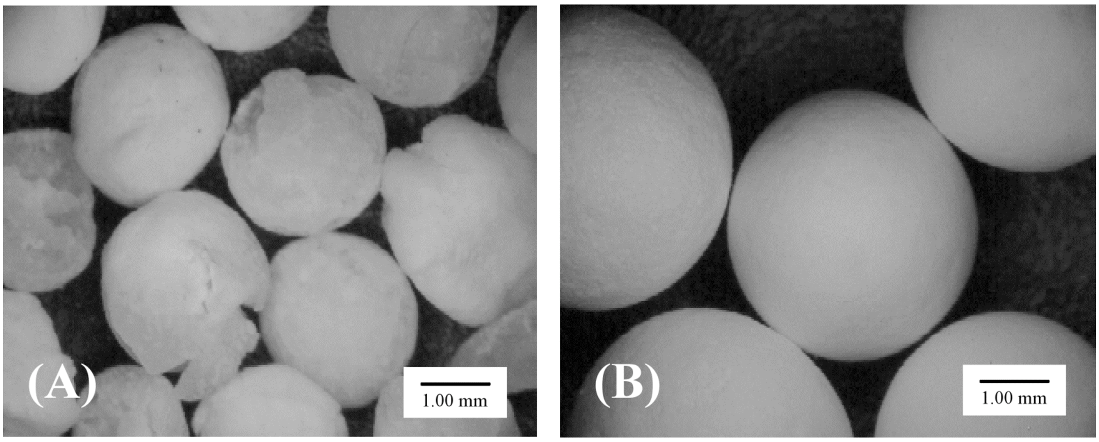

Figure 2. Optical micrograph photograph of (A) Beads from pasty prepolymer, [β-CyD/HDI(1/2)]/HDI and (B) Beads from powdery prepolymer, [β-CyD/HDI(1/8)]/HDI.

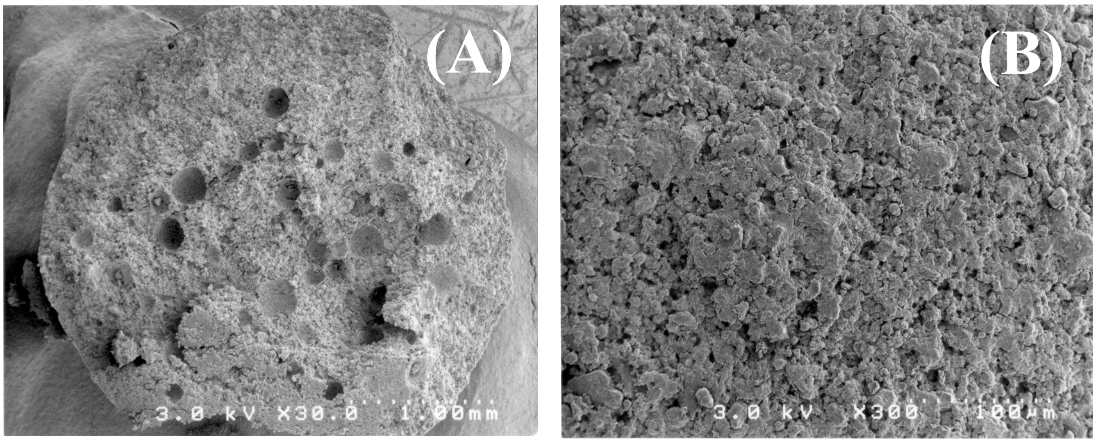

Figure 3. SEM pictures of transverse (A) and surface layer (B) of the [β-CyD/HDI(1/8)]/HDI bead polymer.

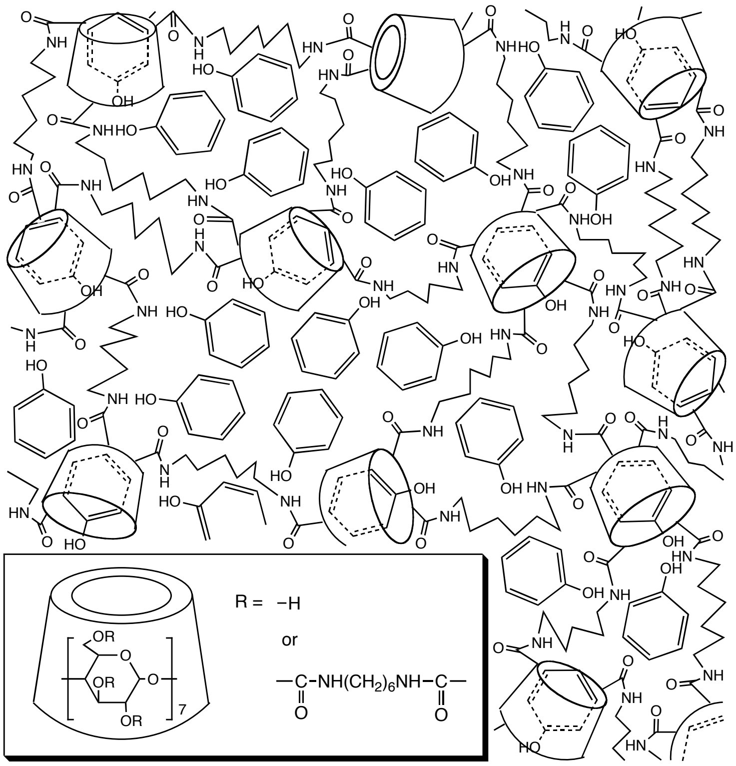

Figure 4. Scheme of the image for the adsorbed phenol onto the β-CyD polymer beads in aqueous industrial wastewater discharged from phenolic resin processing.

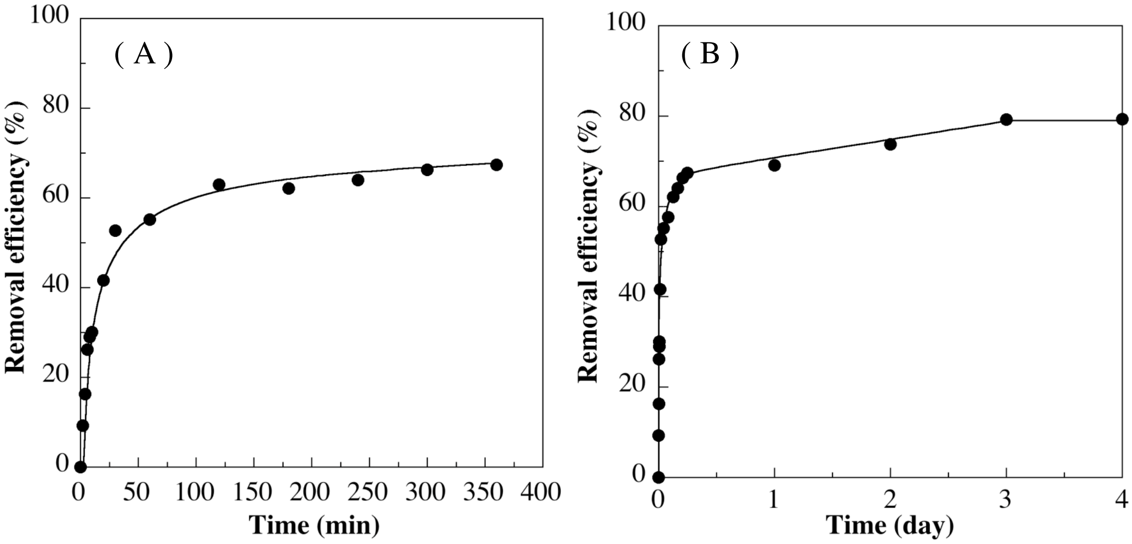

Figure 5. Time plots of the removal of phenol with [β-CyD/HDI(1/8)]/HDI sorbent (1.0 g) from phenolic wastewater solution (5 cm^3) at 25°C. (A) for 6 h, (B) for 4 days.

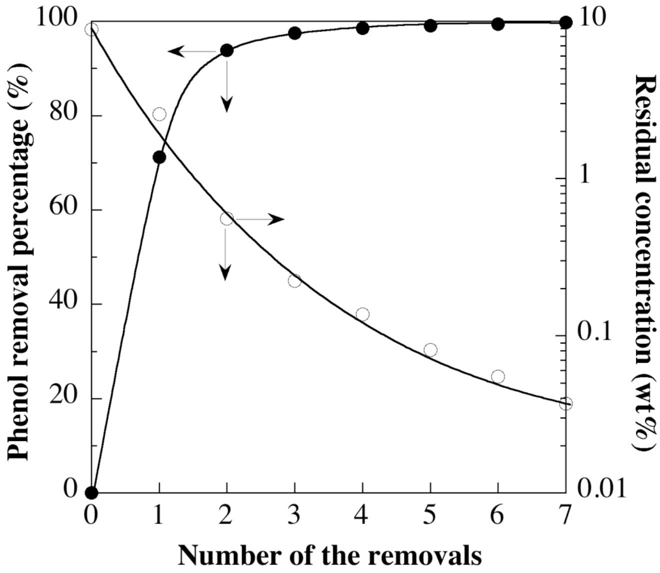

Figure 6. Repetition of the removal of phenol with [β-CyD/HDI(1/8)]/HDI polymer beads in batchwise adsorption: Each adsorption was carried out by placing a fresh adsorbent (1.0 g) and wastewater solution (5 cm^3), from which the previous adsorbents were filtered off, in a 50-cm^3 Erlenmeyer flask and shaking it at 25°C in a chamber at 80 rpm for 1 day.

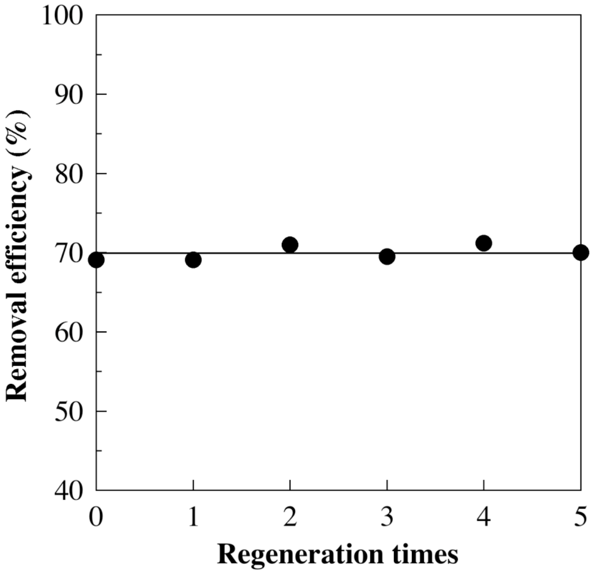

Figure 7. Removal of phenol from wastewater solution with the regenerated [β-CyD/HDI(1/8)]/HDI sorbent: Each adsorption was carried out by placing the regenerated adsorbent (1.0 g) and wastewater solution (5 cm^3) in a 50-cm^3 Erlenmeyer flask and shaking it at 25°C in a chamber at 80 rpm for 1 day.

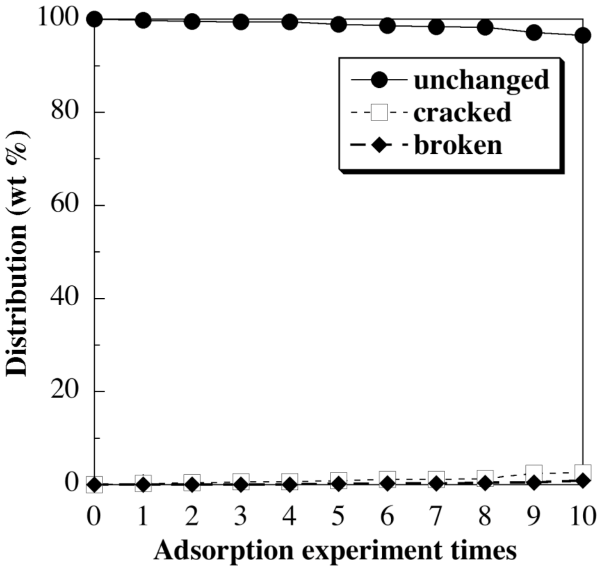

Figure 8. Mechanical stability of the [βCyD/HDI(1/8)]/HDI polymer beads in batchwise adsorption.

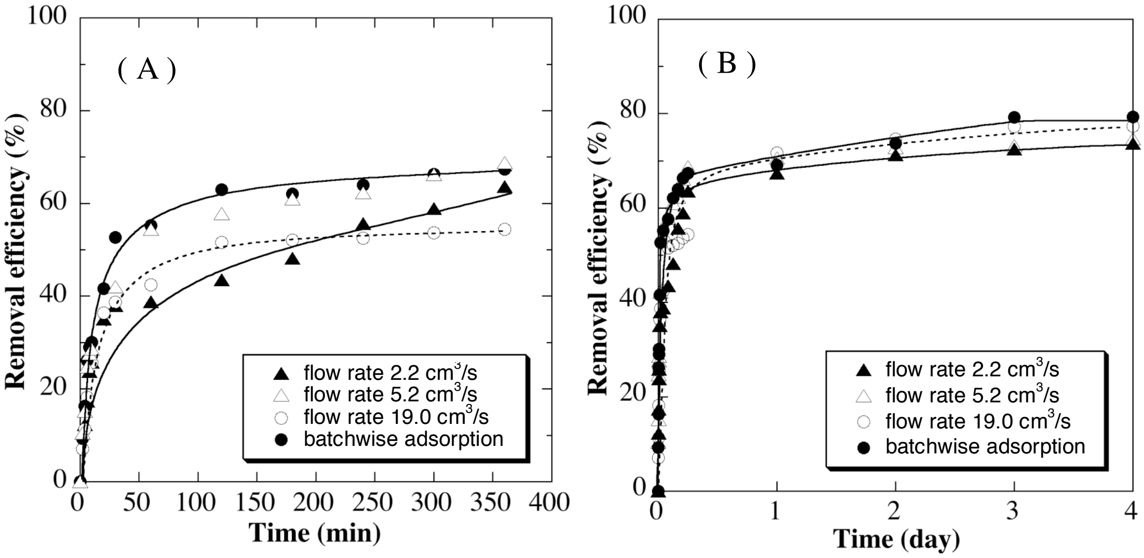

Figure 9. Efficiency of phenol removal ratio with upflow column at different circulation flow rates. (A) 6 h, (B) 4 day.

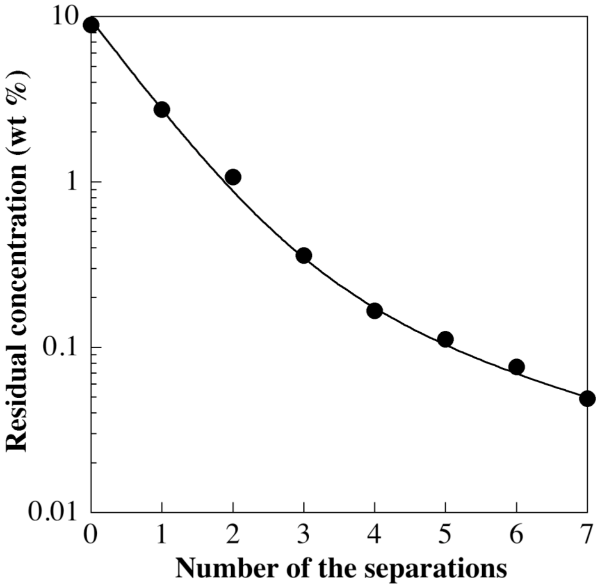

Figure 10. Repetition of the separation of phenol with the β-CyD polymer beads in an upflow column. Each adsorption was carried out by placing the regenerated adsorbent (25 g) and wastewater solution (125 cm^3) in an upflow column circulating at a flow rate of 5.2 cm^3/s at 25°C for 1 day.