

Removal of phenolic compounds from aqueous solution by β -cyclodextrin polymer

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We investigated the adsorption and desorption of phenolic compounds such as 4-nonylphenol (NP), 4-nonylphenol ethoxylates (NPE), and bisphenol A (BPA), using crosslinked β -cyclodextrin polymer (CDP). According to the adsorption isotherms of these compounds, it was revealed that the adsorption of the NPE onto CDP was dependent on the length of the ethoxylates in the NPE. As the ethoxylate chain of NPE became longer, the adsorption efficiency onto CDP decreased. Column adsorption and desorption tests revealed that the phenolic compounds adsorbed on CDP were successfully released by various kinds of alcohol aqueous solutions. As CDP was also able to be reused, it appeared that CDP was available for the recovery or preventing the effusion of phenolic compounds.

Key words: cyclodextrin, cyclodextrin polymer, phenolic compound, adsorption, recycling system

1. INTRODUCTION

Water contamination by phenolic compounds has widely spread and the contaminants have been detected in water and sediments [1]. For example, 4-nonylphenol (NP) and bisphenol A (BPA), which are doubted as endocrine disrupters, are mainly used in chemical industry and 4-nonylphenol ethoxylates (NPE) are used as a surfactant in various industries. NPE is frequently dumped in effluent water and biodegraded to NP in rivers or underground water [2]. Hence, it is very important to recover these chemicals and not allow them to effuse into the environment from industrial waste water.

Cyclodextrins (CDs), which are doughnut-shaped cyclic oligosaccharides composed of 6 – 8 glucose residues, have been utilized in various fields, for example, food [3], pharmacy [4], analysis [5] or the environment. CD is well known to have a fascinating property to selectively include some organic compounds. Therefore, various organic pollutants have been investigated for removal from water or air using CD [6–9]. The CD polymer (CDP) crosslinked CD with epichlorohydrin also retains its inclusion property [10], and it has been used as an adsorbent for organic pollutants. The removal techniques or adsorption phenomenon of compounds such as nonionic surfactant [11], phthalic acid esters [12], and aromatic chemicals [13–15], were investigated. Other insoluble CDs, immobilized onto other substances such as silica [16] or chitosan [17], were also investigated as adsorbents of phenolic pollutants.

In this report, the adsorption and desorption of phenolic compounds using CDP were investigated, and the reuse of CDP was also examined in order to develop an ecologically advantageous recycling system for water treatment. In previous reports, though alcohol is inflammable, methanol or ethanol was usually applied for the desorbing solvent [12, 18]. In order to prevent the danger of flashing, it is important to reduce the alcohol amount in the desorption solvent. Thus, the recovery method using small amounts alcohol was also

investigated.

2. EXPERIMENT

2.1 Materials

Analytical grade 4-nonylphenol (NP), 4-nonylphenol ethoxylates (NPE), and bisphenol A (BPA) were purchased from Tokyo Kasei Co., Ltd. NPE has a hydrophobic tail of a nonyl group and a hydrophilic head of ethylene oxide (EO) chain. In this study, we mainly used NPE with $n=5, 10, 15,$ or 20 (n , average number of repeating ethylene oxide units per molecule). β -Cyclodextrin polymer (CDP), crosslinked β -CD with epichlorohydrin, was a product of Bio Research Corporation of Yokohama Co., Ltd. It was almost spherical in shape, and its diameter ranged from about 0.1 to 2 mm; its presumed β -CD mole equivalent was 0.55 mmol/g. CDP was rinsed twice in diluted water and once in methanol before use.

2.2 Batch adsorption tests

The batch adsorption tests were performed in flasks to which 100 mL of aqueous solution containing the phenolic compounds (concentration 0~1 mmol/L) and 0.1 g of β -CDP were added. The flasks were shaken at room temperature. The residual amount of the organic solute in the flask was determined by UV-spectrophotometry (Hitachi spectrophotometer U-3000, Hitachi Co., Ltd.) at each sampling time.

2.3 Column Tests

The continuous column treatment tests were carried out employing a Pyrex tube that was 7 mm in diameter and 150 mm long. It was filled with 0.5 g of CDP on a small portion of glass wool placed at the bottom of the column. An aqueous solution containing 0.15 mmol/L of BPA or NPE ($n=10$) was fed at a 1.8 mL / min rate into the column at room temperature. The effluent from the column was periodically sampled, and each compound's concentration was determined.

2.4 Recovery of the phenolic compounds and reuse of CDP

CDP with previously adsorbed BPA or NPE ($n=10$) was dried at 60°C and then shaken with a 100-fold volume (10 mL/0.1 g) of aqueous alcohol solution. In order to estimate the recovery efficient, methanol, ethanol, 2-propanol and *t*-butanol were examined. The mixture ratio of alcohol and water was varied over the range of 10:0 to 0:10.

The reusability of CDP was confirmed by the adsorption and desorption cycling using the column method. The utilized column was a Pyrex tube of 13 mm diameter and 300 mm length, and was loaded with 3 g of on a small layer of glass wool.

The repetition tests were carried out as follows: One L of an aqueous solution containing 0.15 mmol/L of BPA or NPE ($n=10$) was fed at a 2.0 mL/min rate into the column; A 100 mL aqueous 40% *t*-butanol solution was recycled for 1 h at a 3.0 mL/min rate; Another 100 mL of an aqueous 40% *t*-butanol solution was recycled 1 h again at the same flow rate; The CDP was then rinsed with 100 mL of distilled water before the next adsorption procedure.

3. RESULTS AND DISCUSSION

3.1 Kinetics and Adsorption Isotherm

Figure 1 illustrates the residual ratio of NPE (initial concentration, 0.15 mmol/L) with different average number (n) of ethoxylates units (EO) versus the stirring time. The minimum residual ratio was obtained after 3 h of shaking for NPE of $n=5, 10$ and 15 . It was found that 4 h was sufficient to reach the plateau for NPE of $n=20$. It appeared that the order of the maximum adsorption amount for NPE on CDP was also dependent on the length of the EO chains of NPE. Judging from the rate and the amount of adsorption, the adsorption of NPE occurred more efficiently as the length of EO chains of NPE became shorter and the order is as follows: $n=5 > n=10 > n=15 > n=20$.

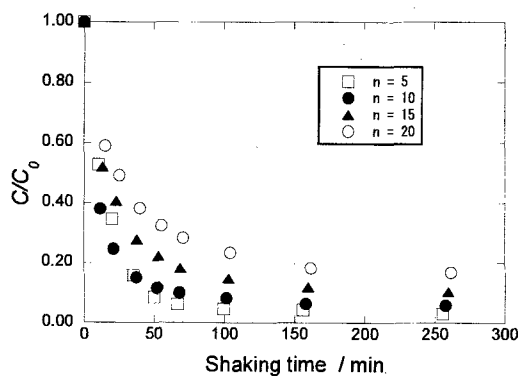


Figure 1 Dependence of the relative concentration of NPE on the shaking time in 100 mL of aqueous solution containing 0.15 mmol/L of NPE with 0.1 g of CDP at room temperature.

The adsorption isotherms for NPE were fitted to the Langmuir isotherm in the relation between C versus C/q (Figure 2), where C is the equilibrium concentration and

q is the adsorption capacity on CDP. The equations obtained from Figure 2 are as follows: $n=5$: $C/q = 0.0029 C + 0.277$, $R = 0.989$; $n=10$: $C/q = 0.0036 C + 0.213$, $R = 0.996$; $n=15$: $C/q = 0.0043 C + 0.250$, $R = 0.999$; $n=20$: $C/q = 0.0084 C + 0.3844$, $R = 0.998$, where R is the correlation coefficient. The linear representation of the Langmuir isotherm is

$$C/q = 1/bQ + C/Q \quad (1)$$

where Q ($\mu\text{mol/g}$) is the limiting adsorption capacity [18], and b ($\text{L}/\mu\text{mol}$) is a constant related to the energy of adsorption. Q and b are calculated from the Langmuir isotherm equations and the results are listed in Table 1. The parameters confirmed the adsorption behavior observed in Figure 1. As the analyzed molar amount of β -CD in 1 g of CDP was 612 μmol , the limiting adsorption capacity for NPE was estimated to be under 56% of the molar amount of the β -CD residue in CDP. The linear correlation in the Langmuir plots is usually interpreted that the adsorption is due to the formation of a monolayer of adsorbate on an adsorbant. Judging from the observations described above, it was suggested that the adsorption onto CDP mainly depended on the inclusion phenomenon by the CD cavities [16]. This mechanism can explain the fact that the decrease in apparent adsorption capacity inversely varied with increasing the length of the EO chains because the stability constants in the formation of inclusion complex probably decrease with an increasing hydrophilicity to prolong the EO chain.

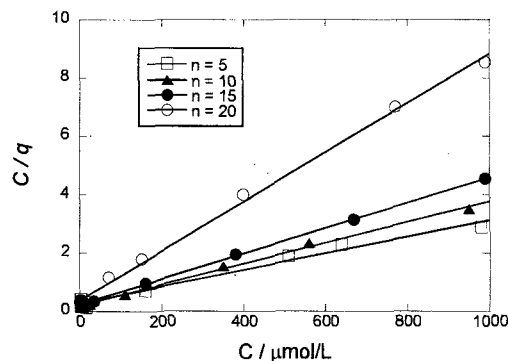


Figure 2 Langmuir adsorption isotherm of NPE on CDP, C is the equilibrium concentration, and q is the adsorption capacity on CDP ($\mu\text{mol/g}$).

Table 1 The constants Q and b of Langmuir adsorption isotherm in equation (1)

Phenols	Q ($\mu\text{mol/g}$)	b ($\text{L}/\mu\text{mol}$)
NPE ($n=5$)	345	0.0105
NPE ($n=10$)	278	0.0169
NPE ($n=15$)	232	0.0173
NPE ($n=20$)	119	0.0219
BPA	714	0.0257
NP	625	0.0157

The constants were calculated in terms of the Langmuir adsorption isotherms plotted in Figure 2 and 3.

On the other hand, with regard to NP and BPA, shaking for 2 h attained equilibrium, and they were more rapidly adsorbed than NPE. The equations obtained from Figure 3, which illustrates the Langmuir adsorption isotherm, are as follows: BPA: $C/q = 0.0014 C + 0.054$, $R = 0.952$; NP: $C/q = 0.0016 C + 0.102$, $R = 0.573$, respectively. A linear correlation in the Langmuir plots for BPA was not so good as for NPE. And the data for NP was relatively scattered in comparison with other phenolic compounds investigated in this study. The constants Q and b of these compounds, obtained from equation (1), are also listed in Table 1. The limiting adsorption capacity for BPA and NP were estimated to be 116 % and 102 % of the molar amount of the β -CD residue in CDP, respectively.

CDP has mainly two kinds of adsorption sites consisting of a CD cavity and a polymer network introduced by epichlorohydrin. In previous papers, benzene, alkylbenzenes and phenol were reported to be adsorbed on the network of CDP [13, 15]. As for BPA and NP, because of the correlation in the Langmuir isotherm and the limiting adsorption capacity beyond the capacity calculated from CD content, it assumed that they would be adsorbed by other interactions, such as, the polymer network or between adsorbed molecules, addition to the inclusion mechanism [16].

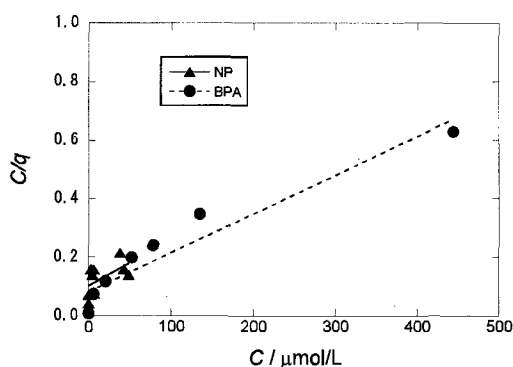


Figure 3 Langmuir adsorption isotherms of BPA and NP on CDP, C is the equilibrium concentration, and q is the adsorption capacity on CDP ($\mu\text{mol/g}$).

3.2 Column tests

The breakthrough curves for BPA and NPE ($n=10$) are plotted in Figure 4. The results suggested that a larger amount of BPA was adsorbed on CDP compared to NPE. The breakthrough capacities, defined as the effluent volume at which the relative concentration became 1%, were 1200 mL for BPA and 100 mL for NPE. Thus the breakthrough capacity ratio of BPA/NPE was almost 12.

The difference in the breakthrough capacity could be interpreted to be due to the adsorption rate of BPA being more rapid than that of NPE. This suggests that a compound having a small adsorption rate or capacity such as NPE should be treated over a long contact time with CDP by a large column volume or a proper flow rate.

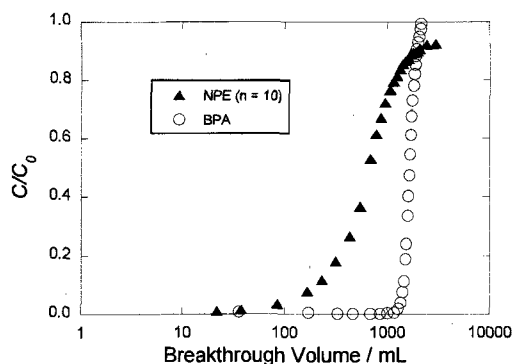


Figure 4 Breakthrough curves of BPA and NPE ($n=10$) for CDP. C and C_0 are the effluent and influent concentrations of BPA or NPE, respectively. 3 g of CDP was loaded on the column and each influent concentration (BPA or NPE) was 0.15 mmol/L.

3.3 Recovery Efficiency

A practical method of recovering BPA or NPE ($n=10$) was carried out using on aqueous alcohol solution. The recovery ratio for each solution was calculated based on the ratio of the recovered amount of the compounds relative to the amount previously adsorbed on CDP. The solution that could recover more than 90 % of the compounds from CDP is shown in Table 2. The recovery efficiency significantly depended on the alcohol/water ratio. The solution that obtained a high recovery efficiency and contained the least amount of alcohol was the aqueous 40% *t*-butanol solution. Though it contained half of alcohol volume compared with aqueous methanol, the recovery efficient was almost the same. Thus a solution of 40 % *t*-butanol and 60% distilled water was used for the recovery of the phenolic compounds from CDP in column recycle tests.

Table 2 Alcohol ratio obtained for over 90 % of recovery efficiency of BPA and NPE from CDP

Alcohol	Alcohol ratio (%)	
	BPA	NPE
Methanol	Above 80	80-90
Ethanol	60-80	70-80
2-Propanol	50-80	50-70
<i>t</i> -Butanol	30-50	30-40

β -CDP, previously adsorbed BPA or NPE, was shaken for 2 h with 100 times volume of aqueous alcohol solution.

3.4 Column recycle tests

The column recycle test for adsorption and desorption of BPA or NPE was repeated 20 times. The results of the adsorption efficiency are shown in Table 3, and the recovery amount of the compound was larger than 90 % for each run.

On the other hand, though activated carbons are

effective for the adsorption of phenolic compounds, it is not very easy to release and reuse the adsorbate. To release the phenolic compounds from activated carbons, the atmospheric temperature had to be maintained in the range of 600-900K [20].

Table 3 Adsorption ratio of BPA and NPE(n=10) on CDP for repeated runs

Repetition times	Adsorption ratio (%)	
	BPA	NPE
0	100	95
5	99	96
10	100	95
20	98	95

The repetition test of adsorption and desorption was performed using the column technique loaded with 3 g of CDP.

In the case of treating actual industrial drainage, a column treatment system is usually more convenient than a batch adsorption system. Furthermore, it is useful for the adsorbent to be regenerated in the column without being removed from the equipment. It was confirmed that CDP was an appropriate adsorbent for recycling use as the operation of adsorption and desorption on the column was able to handle it with ease.

4. CONCLUSION

In the adsorption of NPE onto CDP, adsorption behavior agreed with the Langmuir isotherm, therefore, it was confirmed that NPE was mainly adsorbed by inclusion mechanism.

On the other hand, as the adsorption of NP did not show obvious correlation in the Langmuir isotherm and the limiting adsorption capacities of BPA and NP exceeded the value expected from CD content, it was assumed that BPA and NP were adsorbed on the crosslinking site of CDP or by the interaction between adsorbed molecules, addition to the inclusion.

An aqueous 40 % *t*-butanol solution was found to be able to release and recover the phenolic compounds from CDP at almost the same efficiency as aqueous 80 % methanol. The solution uses a small amount of alcohol and decreases the danger of flashing.

A suitable method capable of repeating the adsorption and desorption was developed on the column system. The recycle use of CDP was repeated 20 times using the column system, and almost the same adsorption ratio as compared to the initial run was assessed.

It appeared that CDP was suitable as an adsorbent of water treatment in terms of the recycle utilization and the ease of handling. The developed treatment system would be applied with recovering NPE, such as in waste water from the textile industry.

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