

An Efficient Adsorption–Desorption System for Hydrophobic Phenolic Pollutants—Combined Use of Mono-6-amino- α -cyclodextrin and Cation Exchanger

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A simple and efficient method to remove hydrophobic phenolic pollutants from aqueous solutions has been investigated using the inclusion ability and cationic property of mono(6-amino-6-deoxy)- α -cyclodextrin (ACD) and a cation exchanger. The inclusion complexes of nonylphenol and bisphenol A with ACD were almost completely adsorbed onto a column of a cation exchanger and desorbed with diluted aqueous ammonia solution. Moreover, bisphenol A was also adsorbed on a column of the cation exchanger that was pretreated with ACD.

Endocrine disruptor chemicals (EDCs) are contaminations that mimic endogenous hormones and disrupt important life processes such as embryonic development, sexual differentiation, reproduction, and immunity.¹ Although the use of these compounds is globally regulated, the accumulation of these compounds has been observed in greatest quantity in the sediment soil of lakes and/or rivers. Since the solubility of most of the EDCs is low in water, the removal of these compounds from the environment is extremely difficult; however, it poses a crucial problem that must be solved as soon as possible.

Cyclodextrins (CDs) are cyclic oligomers composed of α -D-glucopyranose produced from enzymatic degradation of starch on an industrial scale.^{2,3} Since they have a unique property of including various organic compounds in their hydrophobic cavities, extensive investigations have been carried out to utilize these inclusion complexes in various fields. Recently, the application of CDs to environmental remediation has attracted considerable attention.^{4,5} Some polymer-supported CD derivatives have been reported for the adsorption and desorption of the aromatic pollutants.^{6–8} However, preparation of CD-polymers required tedious synthetic procedures, and organic solvent such as methanol was necessary to desorb EDCs from the polymers. Hence, it is necessary to develop a novel and versatile procedure that can perform both the adsorption and desorption of the pollutants efficiently. In this paper, we describe another efficient approach to remove and concentrate nonylphenol (NP) or bisphenol A (BPA) that are common EDCs containing the phenol moiety. This involves combined use of mono(6-amino-6-deoxy)- α -cyclodextrin (ACD) and the cation exchanger having carboxymethyl groups on the surface of the carrier.

CD derivatives such as hydroxypropyl,⁹ carboxymethyl,¹⁰ and ethyleneglycolyl CDs¹¹ are often used as solubilizers for various hydrophobic compounds. We deduced that ACD, which has cationic property, also improves the solubility of compounds with poor water-solubility. At first, the water-solubility of NP or BPA in aqueous ACD¹² solutions was examined. To a certain concentration (5–80 mmol/L) of ACD solution in deionized water was prepared and small portions of NP or BPA were added. After the solution was equilibrated using a shaker for

24 h at 298 K, the solubility of each EDC was analyzed by a UV–vis spectrometer. UV adsorption at 275 nm was increased linearly with increasing the amounts of EDCs and became constant. The relationship between the concentration of the ACD and the solubilities of NP and BPA is shown in Figure 1. It was evident that the relation between the enhanced solubility of each EDC and the increase in the concentration of the ACD was clearly linear. Since the solubilities of NP and BPA in water are only 6 mg/L (0.027 mmol/L) and 120 mg/L (0.526 mmol/L) in the absence of CD, respectively, it was suggested that the addition of the ACD would lead to a remarkable increase in the water-solubilities of these EDCs. The compositions of the inclusion complexes formed by NP and BPA with the ACD are in the ratio 1:1.4 (ACD:NP) and 1:2.8 (ACD:BPA), respectively. Phenolic compounds, which have poor water-solubility, increase the hydrophilicity by forming inclusion complexes with CD. In general, the composition of the inclusion complexes of phenolic compounds and CD is almost in a ratio of 1:1. However, NP has a long alkyl chain with phenol moiety, and BPA has two phenol moieties within the molecule. Hence, it is obvious that a number of the ACDs include not only the phenol moieties of these EDCs but also their alkyl moieties.¹³

Next, the application to the adsorption–desorption system of EDCs with the ACD was discussed. Herein, CM-Sephadex C-25 (NH_4^+ form)¹⁴ was selected as a cation exchanger to produce an ion complex with the ACD. Figure 2 illustrates the schematic procedures for the formation of the inclusion complexes of EDCs with the ACD onto the cation exchanger. Procedure A shows the adsorption–desorption of the ACD-EDC complexes onto the cation exchanger, whereas procedure B shows an exper-

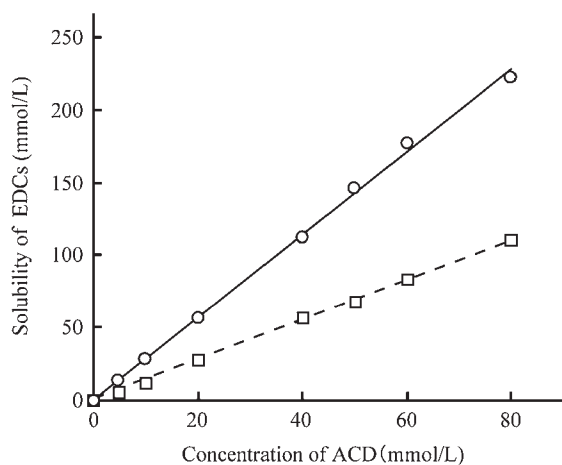


Figure 1. Relationships between the concentration of ACD and the solubility of EDCs. BPA (○); NP (□).

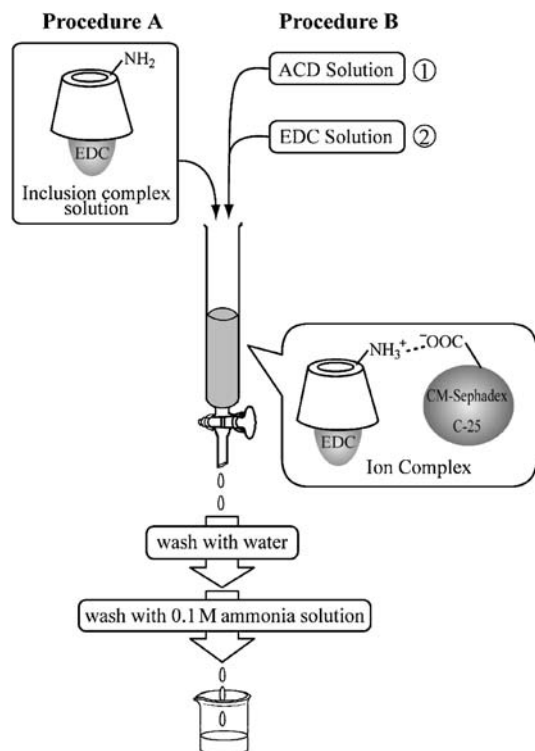


Figure 2. Schematic procedures for removal and recovery of EDCs in this study.

imental setup for the adsorption of EDC onto the ACD that had been ionically linked with the cation exchanger.

According to the procedure A, the inclusion complexes of the ACD (1.0 mmol/L, 4.0 mL) containing a saturated amount of EDC were prepared in a plastic tube and applied to a column of the cation exchanger (i.d. 15 × 100 mm). The column was washed with deionized water (60 mL). Consequently, each ACD–EDC complex was recovered by eluting with aqueous ammonia solution (0.1 mol/L) and lyophilized. The obtained powder was dissolved in 4 mL of deionized water and analyzed by a UV–vis spectrometer. The amount of flow of the EDC was determined from the calibration curve. The recovery ratio of ACD–EDC complexes was calculated from the before and after concentration of each EDC solution. Consequently, the recovery ratio obtained was nearly 100% as shown in Table 1. It was evident that each complex was almost completely trapped onto the cation exchanger and efficiently desorbed by eluting with a basic solvent such as an ammonia solution.

Finally, in order to verify the practical effectiveness of this system, the adsorption–desorption of BPA onto a column of the ion complex of the cation exchanger with the ACD was performed as shown in Figure 2 (procedure B). Unfortunately, NP could not be used in this experiment because of poor water-solubility). The column of the cation exchanger that was ionically linked with the ACD (1.0 mmol/L, 5.0 mL) was first prepared. BPA (50 μmol/L, 5.0 mL) was applied to the column and washed with deionized water (60 mL). The desorption of EDCs from the ACD trapped in the cation exchanger was not almost observed under this condition. Contrastively, elution with aqueous ammonia solution (0.1 mol/L) efficiently desorbed BPA with the

Table 1. Recovery ratios of EDCs obtained from the procedure A and B

Procedure	EDC	Applied concentration ^a (mmol/L)	Recovered concentration ^a (mmol/L)	Recovery ratio (%)
A	NP	2.76	2.72	98.6
A	BPA	1.28	1.24	96.8
B	BPA	5.00×10^{-2}	4.30×10^{-2}	86.0
B	NT	1.00×10^{-1}	7.30×10^{-2}	73.0

^aThe values were measured by UV–vis spectrometer.

ACD from the cation exchanger. The recovery ratio of the BPA was 86% as calculated from the measurement by the UV–vis spectrometer (Table 1). Similarly, when *p*-nitrotoluene (NT), which is one of the EDCs, was used in this system, the ratio obtained was 73%. Thus, it is suggested that the trapping efficiency of EDCs in this system is significantly dependent on their solubility in water, because NT has a relatively high water-solubility (the value is 350 mg/L (2.55 mmol/L)).

In conclusion, an efficient and versatile EDC-removal system, utilizing the inclusion of EDCs into the ACD and adsorption–desorption of the ACD onto the cation exchanger, has been developed. Since the CDs with hydrophobic cavities of different sizes, such as β- or γ-CD derivatives, are available to include a variety of EDCs, this system might be a powerful tool in the selective removal of EDCs from water sources. The application of this system to another EDC is now under investigation and the results will be reported as soon as possible.

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