Adsorptive Removal of Endocrine Disrupting Chemicals by Calix[4]crown Oligomer: Significant Improvement of Removal Efficiency by Oligomerization

Hirohito Tsue,*[1,2] Tatsuya Takimoto,[1] Chieko Kikuchi,[3] Haruna Yanase,[2] Koichi Ishibashi,[2]
Koji Amezawa,[2] Hideaki Miyashita,[1,2] Hisashi Miyafuji,[4] Shunitz Tanaka,[3] and Rui Tamura[1,2]
[1]*Graduate School of Global Environmental Studies, Kyoto University, Kyoto 606-8501*
[2]*Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501*
[3]*Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810*
[4]*Graduate School of Energy Science, Kyoto University, Kyoto 606-8501*

(Received December 12, 2005; CL-051518; E-mail: tsue@ger.mbox.media.kyoto-u.ac.jp)

Adsorptive removal of phenolic endocrine disrupting chemicals by finely powdered calix[4]crown oligomers has been studied. Batch adsorption experiments and electron microscope measurements demonstrated that morphology of the adsorbents played a central role in the control of the present adsorption behavior.

A wide variety of chemicals are currently being released into the natural environment, and some of these chemicals are referred to as "endocrine disrupting chemicals (EDCs)" that can interact with the endocrine systems of many species and affect their growth, reproduction, and development.[1] The presence of EDCs in the environment has been a matter of great concern because of the adverse health and ecological effects. As a natural consequence, efficient processes to remove trace EDCs dispersed in the aquatic environment have attracted considerable attention of scientific communities for the last decade. For this purpose, a number of techniques have so far been investigated, including adsorption, nanofiltration, chemical degradation, biodegradation, and coagulation.[2] When we consider the real environment, however, collection of trace EDCs is crucial for the final destruction of them. We envisaged adsorptive removal as one of the desirable candidates for establishing the efficient enrichment of trace EDCs because of the attractive prospects, i.e., (1) simple operation, (2) no requirement of peculiar external energy, and (3) no generation of degradation products of unknown toxicity. Activated carbon,[2b,3a] sugar-based organo gel,[3b] calix[6]arene polymer,[3c,3d] cyclodextrin polymer,[3e,3f] and quinoline derivative[3g] were examined as adsorbents for the removal of EDCs.

In the course of our study to develop a novel adsorbent applicable to both organic and inorganic pollutants, we recently reported that finely powdered *p-tert*-butylcalix[4]crown-4 **C4C4** (Figure 1) could remove EDC from an aqueous medium through solid–liquid adsorption phenomena which were controlled by hydrophobic and hydrogen-bonding interactions on the solid surface.[4] While the removal mechanism in **C4C4** was clarified, its adsorption capacity toward EDC was not high enough to allow the practical use as an adsorbent. Yilmaz and co-workers reported that oligomerization of **C4C4** increased the transport ability of heavy-metal ions from aqueous phase to organic phase in liquid–liquid extraction experiments.[5b] In the present study, to improve the removal efficiency, we have prepared oligomers **C4C4OL** and **C4C4OH** with low and high molecular weights (Figure 1), respectively, and evaluated their abilities as adsorbents to remove EDCs by solid–liquid adsorption phenomena. Bisphenol A (BPA) and 17β-estradiol (E2) were used here as model contaminants (Figure 1). Interestingly, highly contrastive adsorption behaviors were observed in these calix[4]crown derivatives; **C4C4** and **C4C4OL** exhibited only the moderate adsorptive removal of the EDCs, whereas **C4C4OH** behaved as an excellent adsorbent that could remove the EDCs almost perfectly from water under the experimental conditions examined herein. In this paper, an intriguing adsorption behavior observed in these calix[4]crown derivatives is reported.

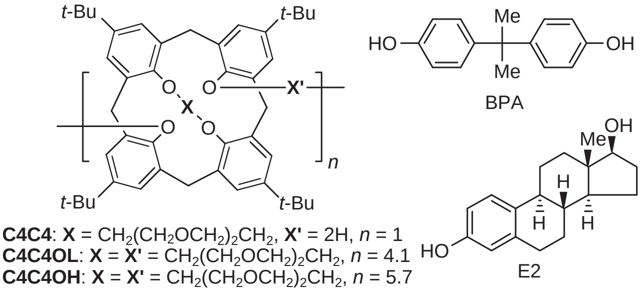

Figure 1. Chemical structures of adsorbents and model EDCs.

Monomer **C4C4** with a cone conformation was synthesized as described.[5] According to the procedure of Yilmaz,[6] **C4C4** was subjected to intermolecular bridging reaction with ethylene glycol ditosylate in the presence of sodium hydride to yield oligomer **C4C4OH** with higher molecular weight. Another novel oligomer **C4C4OL** with lower molecular weight was prepared by the column filtration of the resultant **C4C4OH** through an alumina short plug using CH_2Cl_2/hexane (5:5 then 10:0, v/v) as the eluent. By means of vapor pressure osmometry, the number-averaged molecular weights of the oligomers **C4C4OL** and **C4C4OH** in chloroform at 30 °C were determined to be 3620 ± 30 and 4980 ± 130, respectively, which correspond to $n = 4.1$ and 5.7 in oligomer length (Figure 1; see also Figures S1 and S2, and Table S1 in Supporting Information).

Adsorption abilities of the calix[4]crown derivatives were evaluated by batch adsorption experiments in which finely sieved samples of **C4C4**, **C4C4OL**, and **C4C4OH** with the uniform particle size of 63 µm were used as adsorbents. Aqueous solutions[7] containing 4 mg dm^{-3} of each EDC in 50 cm^3 stopped glass tubes were shaken at 300 rpm for 1 h at 25 °C with 50 molar equivalent amounts of each calix[4]crown derivative.[8] The concentration of the remaining EDC in the filtrate was determined by means of HPLC analysis. Adsorbed ratios (%) of BPA and E2 are summarized in Table 1. In general, depending on the hydrophobicity,[9] greater removal of E2 than BPA was observed.

Table 1. Adsorbed ratio (%) of BPA and E2

EDC	Adsorbent		
	C4C4	**C4C4OL**	**C4C4OH**
BPA	20 ± 2	17 ± 2	94 ± 2
E2	75 ± 7	67 ± 2	94[a]

[a] Standard deviation was not determined.

Besides, the adsorption efficiencies were strongly dependent on the molecular structures of the adsorbents; both **C4C4** and **C4C4OL** showed moderate removal of BPA and E2, whereas **C4C4OH** exhibited an excellent adsorption behavior toward these EDCs.

To throw an insight into the observed difference in the adsorption behaviors, adsorbent characteristics such as surface area, surface property, pore size, and morphology of the calix[4]-crown derivatives were studied. The three adsorbents examined above retained similar and small specific surface areas, which were estimated by means of adsorption of nitrogen gas onto the finely powdered samples at 77 K to give 6.3, 16, and 4.1 $\mathrm{m^2\,g^{-1}}$ for **C4C4**, **C4C4OL**, and **C4C4OH**, respectively (Figure S3 and Table S2). From the chemical point of view, **C4C4OL** and **C4C4OH** must have similar surface property because of their identical skeleton, as reported in our previous paper.[4] Besides, scanning electron microscope (SEM) measurements revealed that all the calix[4]crowns examined here did not have any discernable pores on the solid surfaces at the SEM level, as shown in Figure 2. Nonetheless, an astonishing dissimilarity in morphology was observed in these calix[4]crowns. **C4C4** and **C4C4OL** possessed almost flat and smooth surfaces (Figures 2a and 2b). By contrast, as shown in Figure 2c, **C4C4OH** was composed of a cluster of small particles (ca. 1–5 µm in diameter) although the whole dimension after the particles gathered together was almost the same as those of **C4C4** and **C4C4OL**. Accordingly, it is reasonable to presume that the observed difference in the adsorption behaviors is attributable to the morphology of the adsorbents. At present, fundamental riddles of why only **C4C4OH** affords micrometer-scale particles and of why minor difference in oligomerization degree of **C4C4OL** and **C4C4OH** exerts a large influence on their morphology remain unsolved, but it is experimentally true.

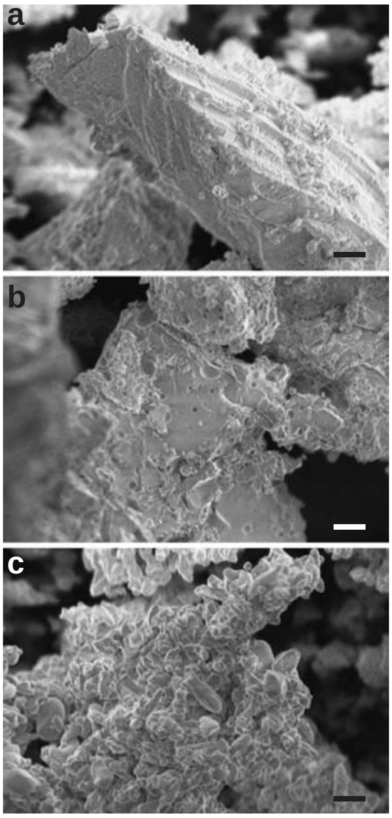

Figure 2. SEM micrographs of (a) **C4C4**, (b) **C4C4OL**, and (c) **C4C4OH**. Scale bar: 5 µm.

In summary, we have demonstrated that oligomerization could much improve the removal efficiency of EDCs from an aqueous medium through solid–liquid adsorption phenomenon. SEM measurements clearly revealed that, among adsorbent characteristics affecting adsorption phenomena, morphology of the adsorbents played a crucial role in the control of the present adsorption behavior. Further study of the removal mechanism is still under progress.

References and Notes

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7 For E2, methanol/water 1:499 (v/v) was used as solvent because of its sparing solubility in water.
8 For **C4C4OL** and **C4C4OH**, used quantities were adjusted in order that the number of calix[4]crown units involved in the oligomer samples was the same as that of monomer to ensure the evaluation of the adsorption behavior of these derivatives with different molecular weights.
9 Octanol–water partition coefficients ($\log K_{\mathrm{OW}}$) of E2 and BPA are reported to be 4.01 and 3.32, respectively, in Ref. 10.
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