Technical Notes

Complete Removal of Chlorinated Aromatic Compounds from Oils by Channel-Type γ-Cyclodextrin Assembly

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This paper describes the complete removal of chlorinated aromatic compounds from insulating oil by a channel-type γ-cyclodextrin (γ-CD) assembly as a new adsorbent. Using this type of adsorbent (50–60 wt % of oil), 1,2,4- and 1,3,5-trichlorobenzenes, 2- and 4-chlorobiphenyls (2- and 4-MCBs), 4,4′-dichlorobiphenyl (4,4′-DiCB), and 3,4,4′-trichlorobiphenyl (3,4,4′-TrCB), whose initial concentrations were 100 ppm, were completely removed from the insulating oil. Competitive adsorption experiments using a mixture of 2-MCB and 4-MCB or a mixture of 4-MCB, 4,4′-DiCB, and 3,4,4′-TrCB revealed that selective adsorption based on the shape and size of the chlorinated aromatics was achieved by the channel-type γ-CD assembly, implying that inclusion into the cavity of the channel-type γ-CD was responsible for the removal of chlorinated aromatics from insulating oil. It was also found that more than 70% of adsorbed chlorinated aromatics was easily recovered from the channel-type γ-CD by simply washing with n-hexane, and chlorinated aromatics were completely removed from the insulating oil even by the regenerated adsorbent, indicating that the γ-CD assembly can be easily regenerated and recycled.

Cyclodextrins (CDs) are a class of cyclic oligosaccharides consisting of several α-(1,4)-linked β-glucopyranose units. They have a hydrophobic cavity into which a guest molecule of an appropriate size and shape can be incorporated. The ability of CDs to form inclusion complexes with organic molecules has found applications in many areas, including the food and pharmaceutical industries and analytical chemistry. However, in most cases, inclusion complex formation in nonpolar organic media would be very difficult, because the main driving force for the inclusion of guest molecules into the CD cavity is hydrophobic interactions, van der Waals interactions between the guest molecules and the CD cavity, or both, and hence, the enormous amount of nonpolar organic solvents becomes a strong competitor against the guest molecules for inclusion into the CD cavity. If a CD derivative were developed that can efficiently form inclusion complexes with guest molecules in nonpolar organic media, then it would open a new area of application for CDs. Such a CD derivative can be expected to allow the selective removal and extraction of persistent organic pollutants such as polychlorobiphenyls (PCBs) from oils.

PCBs were widely used as insulating fluids in capacitors and transformers. Although their manufacture and commercial use have been prohibited in many countries since the 1970s because of their strong toxicity, environmental persistence, and bioaccumulation, large amounts of insulating oils contaminated with PCBs are still being used or are kept without being appropriately treated in many countries, including Japan. In the Stockholm Convention on Persistent Organic Pollutants (see the Web page http://www.pops.int), more than 150 countries have agreed to destroy PCBs until 2025. Thus, the efficient and safe treatment of PCB-contaminated insulating oils is a crucial problem from a global viewpoint.

We report herein that a channel-type γ-CD assembly,13–18 in which γ-CD molecules are stacked in a head-to-head or head-to-tail orientation to form a column in the crystal, can function as an effective adsorbent to remove chlorinated aromatic compounds (including PCBs) from insulating oil via inclusion complex formation. Although Uyar et al. previously reported the preparation of inclusion complexes between channel-type γ-CD assembly and organic compounds such as ethylbenzene, toluene, and propylbenzene in aqueous media,18 and Rusa et al.14 and Uyar et al.16 reported that channel-type α- and γ-CD assemblies formed inclusion complexes with propionic acid and styrene, respectively, in polar organic solvents such as acetone, to the best of our knowledge, there has been no report on the complexation between channel-type CD assemblies and organic molecules in nonpolar organic media. In addition, it was preliminarily examined as to whether the adsorbed compounds could be recovered by washing with organic solvents and if the regenerated adsorbent could show the adsorption capability toward chlorinated aromatics in the insulating oil, in order to assess if the adsorbent could be recycled in practical use.

EXPERIMENTAL SECTION

Reagents. γ-CD was purchased from Junsei Chemical Co., Ltd. Channel-type γ-CD assemblies were prepared and characterized according to the previously reported method.14 In the X-ray diffraction pattern of the prepared γ-CD assembly, a strong peak at 2θ = 7.5°, which was characteristic of the channel structure,14 was observed. Insulating oil was purchased from Taniguchi Petroleum Refining Co., Ltd. 1,2,4-Trichlorobenzene (1,2,4-TrCBz) and 1,3,5-trichlorobenzene (1,3,5-TrCBz) were purchased from Tokyo Chemical Industry Co., Ltd. 2-Chlorobiphenyl (2-MCB), 4-chlorobiphenyl (4-MCB), 4,4′-dichlorobiphenyl (4,4′-DiCB), 3,4,4′-trichlorobiphenyl (3,4,4′-TrCB), and 3,3′,5,5′-tetrachlorobiphenyl (3,3′,5,5′-TeCB) were purchased from AccuStandard, Inc.

Apparatus and Analysis. The quantitative analyses of chlorinated benzenes in insulating oil were carried out with a gas chromatograph–mass spectrometer (GC/MS, QCMS-QP5050, Shimazu) equipped with a DB-1MS capillary column (30 m × 0.25 mm i.d., 0.5-μm film thickness, Agilent Technologies). γ-CD (prepared from CD from Hokkaido) and 4-μm film thickness, Agilent Technologies) was used as an internal standard. The temperature program was 50–100 °C at 10 °C/min, then at 5 °C/min to 180 °C, at 20 °C/min to 325 °C, and then held at 325 °C for 3.75 min. Helium was used as a carrier gas, and both the injector and transfer line temperatures were maintained at 260 °C.

The analyses of chlorinated biphenyls were performed by a high-resolution gas chromatograph (HP 5890 series II, Hewlett-Packard) mass spectrometer (JMS-700, JEOL). The target compounds were quantified by 13C isotope dilution operating in the selected ion monitoring mode. The column used was an HP Ultra 2 capillary column (25 m × 0.2 mm i.d., 0.33-μm film thickness, Hewlett-Packard). The column temperature was programmed from 120 (2 min) to 300 °C (0 min) at a rate of 6 °C/min. Helium was used as a carrier gas, and both the injector and transfer line temperatures were maintained at 260 °C.

Procedure for Adsorption of Chlorinated Aromatics. The prescribed amount of channel-type γ-CD assembly was added into the insulating oil (300 mg) including chlorinated aromatics (100 ppm), and the resulting mixtures were shaken (60 min−1 frequency, 30 mm amplitude) for a certain period of time at 20 °C with a shaker (T-2S, Thomas Kagaku Co., Ltd.). After removal of the channel-type CD (solid) by filtration using a syringe equipped with a filter paper, the concentrations of chlorinated aromatics remaining in the insulating oil were reanalyzed by the above-mentioned GC/MS analyses.

Procedure for Recovery of Adsorbed Compounds. n-Hexane (1 mL) was poured into the syringe used in the above-mentioned experiment and was passed through the channel-type γ-CD (containing the chlorinated aromatics) pile on the filter paper. The amounts of chlorinated aromatics eluted with n-hexane were analyzed by the GC/MS method.

Procedure for Adsorption of Chlorinated Aromatics with Regenerated Adsorbent. The channel-type γ-CD adsorbent was regenerated by washing the chlorinated aromatics-adsorbed one, which was produced by the adsorption experiment, with n-hexane and then drying it overnight at ambient temperature. The adsorption of chlorinated aromatics in insulating oil with the regenerated adsorbent was carried out in the same manner as mentioned above.

RESULTS AND DISCUSSION

First, the adsorption capability of a channel-type γ-CD assembly toward 1,2,4-TrCBz and 3,4,4′-TrCB in insulating oil was examined. Figure 1 shows the removal efficiency of 1,2,4-TrCBz and 3,4,4′-TrCB from the insulating oil as a function of the amount of...
channel-type γ-CD assembly added. Here, the removal efficiency was expressed as the percentage of chlorinated aromatics removed from the insulating oil. The removal efficiency of 1,2,4-TrCBz and 3,4,4′-TrCB increased with an increase in the amount of channel-type γ-CD added. It is noteworthy that 1,2,4-TrCBz and 3,4,4′-TrCB were completely removed when more than 150 mg of channel-type γ-CD (more than 50 wt % of insulating oil) was added. A comparison of the removal efficiency between 1,2,4-TrCBz and 3,4,4′-TrCB showed that 1,2,4-TrCBz was more easily adsorbed by this γ-CD assembly. On the other hand, native γ-CD, which has been reported to adopt a cage-type packing structure in the crystal, showed no adsorption of these chlorinated aromatics in the insulating oil, thus suggesting that the channel structure of γ-CD was essential for the adsorption of chlorinated aromatics. It has been reported that, in the cage-type γ-CD assembly, the cavity space to accommodate the guest molecule is significantly reduced by the insertion of two glucose units of the adjacent molecule from the secondary hydroxyl side. This reduction of the effective cavity space may cause no adsorption of the chlorinated aromatics in the insulating oil by the cage-type γ-CD. The difference in the adsorption of chlorinated aromatics from the insulating oil between the channel-type γ-CD assembly and native γ-CD (cage-type assembly) may also be explained by considering the difference in dispersibility in insulating oil between these two assemblies: on standing the mixture of each CD assembly and insulating oil after shaking for 5 min, the cage-type γ-CD began to precipitate immediately and precipitated completely within 3 h, whereas the channel-type γ-CD stably dispersed in insulating oil without any precipitation for more than 3 days. This improvement in the dispersibility in insulating oil due to the transformation from the cage to the channel structure may allow the γ-CD cavity to effectively come into contact with the chlorinated aromatic molecules in insulating oil, resulting in the complete adsorption of them.

The effect of the shaking time on the removal efficiency of 1,2,4-TrCBz and 3,4,4′-TrCB in insulating oil was also examined (Table 1). The removal efficiency of 1,2,4-TrCBz and 3,4,4′-TrCB increased with an increase in the shaking time. Complete removal of these chlorinated aromatics (100 ppm) from the insulating oil (300 mg) by the channel-type γ-CD (180 mg) was accomplished after shaking for 12 h. 1,2,4-TrCBz was adsorbed more rapidly than 3,4,4′-TeCB. After 1 h of shaking, 85% of 1,2,4-TrCBz was removed from insulating oil, whereas only 50% was removed in the case of 3,4,4′-TrCB. This trend is consistent with the above-mentioned result that 1,2,4-TrCBz complexes with the channel-type γ-CD more easily than 3,4,4′-TrCB.

The order of adsorption selectivity among 4-MCB, 4,4′-DiCB, and 3,4,4′-TrCB was as follows: 4-MCB > 4,4′-DiCB > 3,4,4′-TrCB. This order indicated that the steric hindrance of chlorinated biphenyls affected their adsorption by the channel-type γ-CD. Next, the adsorption capability of the channel-type γ-CD toward various chlorinated aromatics was evaluated (Figure 2). Interestingly, 1,3,5-TrCBz, 2-MCB, 4-MCB, and 4,4′-DiCB, in addition to 1,2,4-TrCBz and 3,4,4′-TrCB, were completely removed from the insulating oil by the channel-type γ-CD. On the other hand, 3,3′,5,5′-TeCB was scarcely removed. This phenomenon can be rationalized by considering that the molecular sizes of 1,3,5-TrCBz, 2-MCB, 4-MCB, 4,4′-DiCB, and 3,4,4′-TrCB are appropriately fitted to the cavity size of the channel-type γ-CD, whereas 3,3′,5,5′-TeCB was too large to be incorporated into the cavity. These results support the hypothesis that inclusion into the cavity of the channel-type γ-CD was responsible for the removal of chlorinated aromatics from the insulating oil. Taking into consideration that large fractions of global PCB stockpiles to be treated consist of tetra- and higher chlorinated biphenyls, the adsorption capability of the present channel-type γ-CD toward PCBs is insufficient for practical use and its modification is required.

In order to obtain more information on the adsorption selectivity of the channel-type γ-CD toward various chlorinated aromatics, competitive adsorption experiments using a mixture of 2- and 4-MCB or a mixture of 4-MCB, 4,4′-DiCB, and 3,4,4′-TrCB were carried out (Figure 3). 4-MCB was adsorbed in preference to 2-MCB by the channel-type γ-CD, indicating that the size or shape of 4-MCB was better fitted to the cavity of the channel-type γ-CD. The order of adsorption selectivity among 4-MCB, 4,4′-DiCB, and 3,4,4′-TrCB was as follows: 4-MCB > 4,4′-DiCB > 3,4,4′-TrCB. This order indicated that the steric hindrance of chlorinated biphenyls affected their adsorption by the channel-type γ-CD assembly.

Preliminary experiments on the recovery of adsorbed chlorinated aromatics from the channel-type γ-CD assembly revealed that more than 70% of the adsorbed chlorinated aromatics was easily recovered from the channel-type γ-CD by simply washing.

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Table 1. Time-Dependence of Removal Efficiency of 1,2,4-TrCBz and 3,4,4′-TrCB from Insulating Oil

<table>
<thead>
<tr>
<th>shaking time (h)</th>
<th>1,2,4-TrCBz (%)</th>
<th>3,4,4′-TrCB (%)</th>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>100</td>
</tr>
<tr>
<td>24</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

* At 20 °C in the presence of 180 mg of channel-type γ-CD assembly.

* The removal efficiency is expressed as the percentage of chlorinated aromatics removed from the insulating oil. * The initial concentrations of 1,2,4-TrCBz and 3,4,4′-TrCB in insulating oil (300 mg) were 100 ppm.
with n-hexane. Additionally, the adsorption experiments toward 1,2,4-TrCBz and 4-MCB with the regenerated γ-CD assembly showed that these chlorinated aromatics were completely removed from the insulating oil even by the regenerated adsorbent. These results indicate that the γ-CD assembly can be easily regenerated and recycled. The present channel-type γ-CD showed little adsorption capability for bulky PCBs such as 3,3′,5,5′-TeCB. Since large fractions of global PCB stockpiles to be treated are tetra- and higher chlorinated biphenyls, the modification of this CD assembly is crucial for practical use as an adsorbent for PCBs in oils. The optimization of the preparation conditions for the channel-type γ-CD assembly and the use of the channel-type assembly from appropriately modified γ-CD would result in the complete removal of any type of PCB, including bulky 3,3′,5,5′-TeCB, from the insulating oil. Such materials can serve as highly effective adsorbents for PCBs in oils and thus significantly contribute to environmental protection. Additionally, these adsorbents may be applicable to the analysis of trace amounts of organic pollutants in oils. Further studies along these lines are now in progress.

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