REMOVAL OF CHLORINATED AROMATIC COMPOUNDS FROM INSULATING OILS BY CHANNEL-TYPE CYCLODEXTRIN ASSEMBLY

Toshiyuki Kida[1], Yoshinori Fujino[1], Kazuhiro Miyawaki[2], Eiichi Kato[2], Chisato Matsumura[3], Takeshi Nakano[3], and Mitsuru Akashi[1]

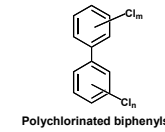
[1]Graduate School of Engineering, Osaka University, Suita 565-0871, Japan; [2]Central Research Laboratory, NEOS Company Limited, Konan 520-3213, Japan; [3]Hyogo Prefectural Institute of Public Health and Environmental Science, Kobe 654-0037, Japan

Introduction

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, 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, 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.

Polychlorinated Biphenyls (PCBs) in Japan



Polychlorinated biphenyls (PCB)

- Excellent Insulating Capacity
- Water-insoluble
- Non-flammability
- High Chemical Stability

PCBs were widely used as insulating fluids in transformers and capacitors.

High Toxicity to the Human Body and the Environment was revealed. (Yusho Incident in 1968)

Large amounts of PCBs have been stored for more than 30 years without treatment.

PCB Treatment Law (2001)

Total Abolition of PCBs until 2016

In 1972 Prohibition of PCB Production and Use by Administrative Direction

In 1974 Prohibition of PCB Production, Imports, and Use by Law

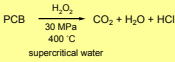
In 1998 Permission of PCB Treatment to Render Harmless by Law

Large amounts of insulating oils contaminated with trace amounts of PCBs (1-100 ppm) are still stored.

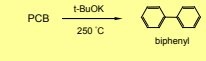
Treatment of PCB-contaminated Oils in Japan

Various chemical destruction methods for PCB-contaminated oils have been developed.

Supercritical Water Oxidation[1]



Dechlorination with Alkalines[2]



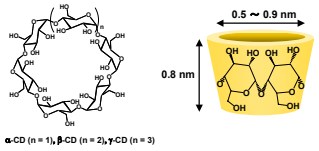
[1] Hatakeda, K. et al., *Chem. Eng. Sci.* **1999**, *54*, 3079.
[2] Ohno, M. et al., *Organohalogen Compounds* **1997**, *31*, 415.

Disadvantage

High reaction temperature and/or prolonged reaction times were required.

Development of New Technique for Efficient Treatment of Large Amounts of PCB-contaminated Oils (More than 500,000 t)

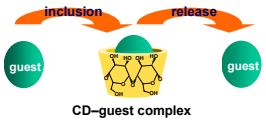
Cyclodextrins (CDs)



α-CD (n = 1), β-CD (n = 2), γ-CD (n = 3)

CDs have a hydrophobic cavity into which compounds of an appropriate size and shape can be incorporated.

Inclusion of Guest Compounds by CD in Aqueous Media



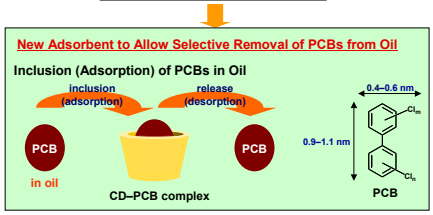
CD–guest complex

Strategy

- The nanoenvironment of CD cavity is comparable to that of 1,4-dioxane.
- The size and shape of PCBs are suitable to be incorporated into the CD cavity.

Appropriate Modification of CDs

New Adsorbent to Allow Selective Removal of PCBs from Oil



Objectives of This Work

Examination of Adsorption Ability of Channel-Type γ-Cyclodextrin Assembly towards Chlorinated Aromatic Compounds (including PCBs) in Insulating Oil

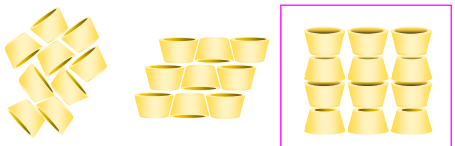
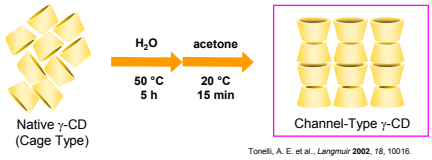


Figure. Schematic representation of packing structures of cyclodextrins in the crystals.

Preparation of Channel-Type γ-CD Assembly



Tonelli, A. E. et al., *Langmuir* **2002**, *18*, 10016.

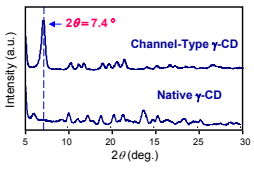
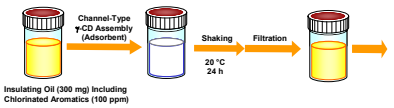
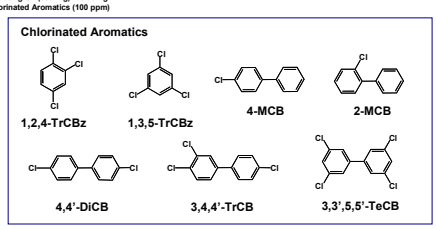


Figure. XRD patterns of channel-type γ-CD and native γ-CD.

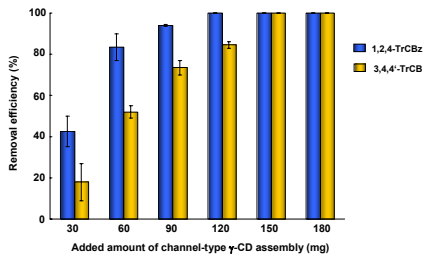
Adsorption Experiments



Chlorinated Aromatics

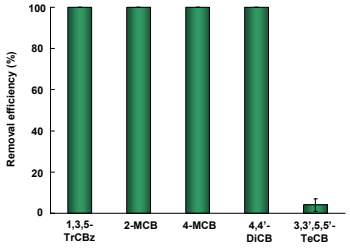


Removal Efficiency of Chlorinated Aromatics as a Function of the Amount of Channel-Type γ-CD



- The removal efficiency (removal percentage) of 1,2,4-TrCBz and 3,4,4′-TrCB increased with an increase in the amount of added channel-type γ-CD. These chlorinated aromatics (100 ppm) were completely removed from insulating oil by the addition of 150 mg of channel-type γ-CD.

Removal Efficiency of Various Chlorinated Aromatics from Insulating Oil*



*180 mg of channel-type γ-CD was used.

- 1,3,5-TrCBz, 2-MCB, 4-MCB, and 4,4′-DiCB were completely removed from insulating oil by channel-type γ-CD. On the other hand, bulkier 3,3′,5,5′-TeCB was scarcely removed.
- Native γ-CD showed no adsorption of these chlorinated aromatics in Insulating oil.

Competitive Adsorption Experiments Using a Mixture of Different Chlorinated Aromatics

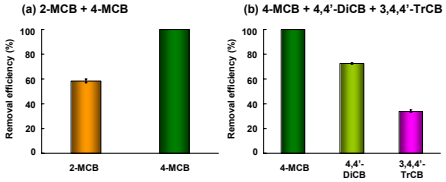


Figure. Removal efficiency of each compounds from insulating oil containing: (a) a mixture of 2-MCB and 4-MCB; and (b) a mixture of 4-MCB, 4,4′-DiCB, and 3,4,4′ TrCB. The initial concentration of each chlorinated aromatic compound was 100 ppm. 120 mg of channel-type γ-CD was used.

The order of adsorption selectivity: 4-MCB > 2-MCB
4-MCB > 4,4′-DiCB > 3,4,4′-TrCB

The steric hindrance of chlorinated biphenyls affected their adsorption by channel-type γ-CD.

Conclusions

- The channel-type assembly of γ-CD functioned as an effective adsorbent to remove chlorinated aromatics from insulating oil.
- Competitive adsorption experiments 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.

Kida, T. et al., *Anal. Chem.* **2008**, *80*, 317-320.

Acknowledgments

This work was supported by a grant for the Promotion of Environmental Technology and Development from the Ministry of the Environment of Japan.