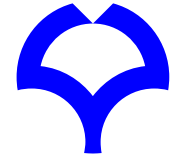


JUNBA 2009

January 13, 2009

Marriott San Francisco Airport, Burlingame

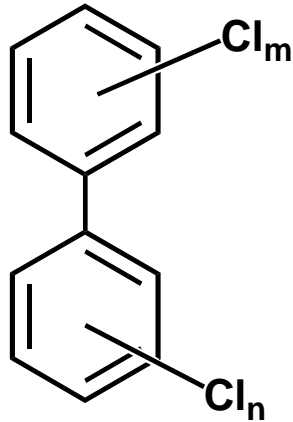


A Technique for Efficient Removal and Recovery of Polychlorinated Biphenyls (PCBs) from Oils

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Graduate School of Engineering, Osaka University

Polychlorinated Biphenyls (PCBs) in Japan



Polychlorinated Biphenyls (PCBs)

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

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



Transformer



Capacitor

High toxicity to the human body and the environment was revealed (Yusho incident in 1968).

Large amounts of PCBs have been stored by the holders 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

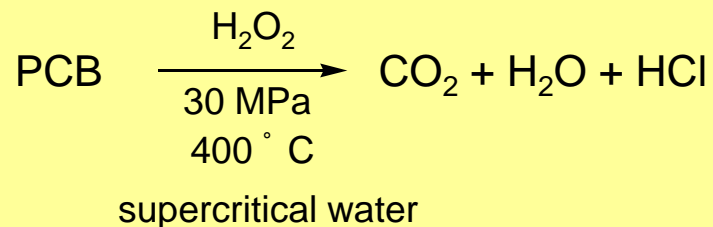
In 1998 Permission of Chemical Destruction Methods to Render PCB Harmless by Law

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

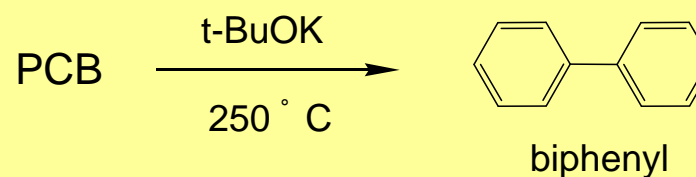
Treatment of PCB-contaminated Oils in Japan

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

Supercritical Water Oxidation¹



Dechlorination with Alkalines²



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

PCB Waste Treatment Facilities of Japan Environmental Safety Corporation (JESCO)



JESCO's Tokyo Facility for PCB Waste Treatment

Table. Capacity for PCB-Contaminated Oil Treatment in JESCO's Five Facilities

	Kitakyushu	Osaka	Toyota	Tokyo	Hokkaido
Capacity	1.3 t/day	2.0 t/day	1.6 t/day	2.0 t/day	1.8 t/day

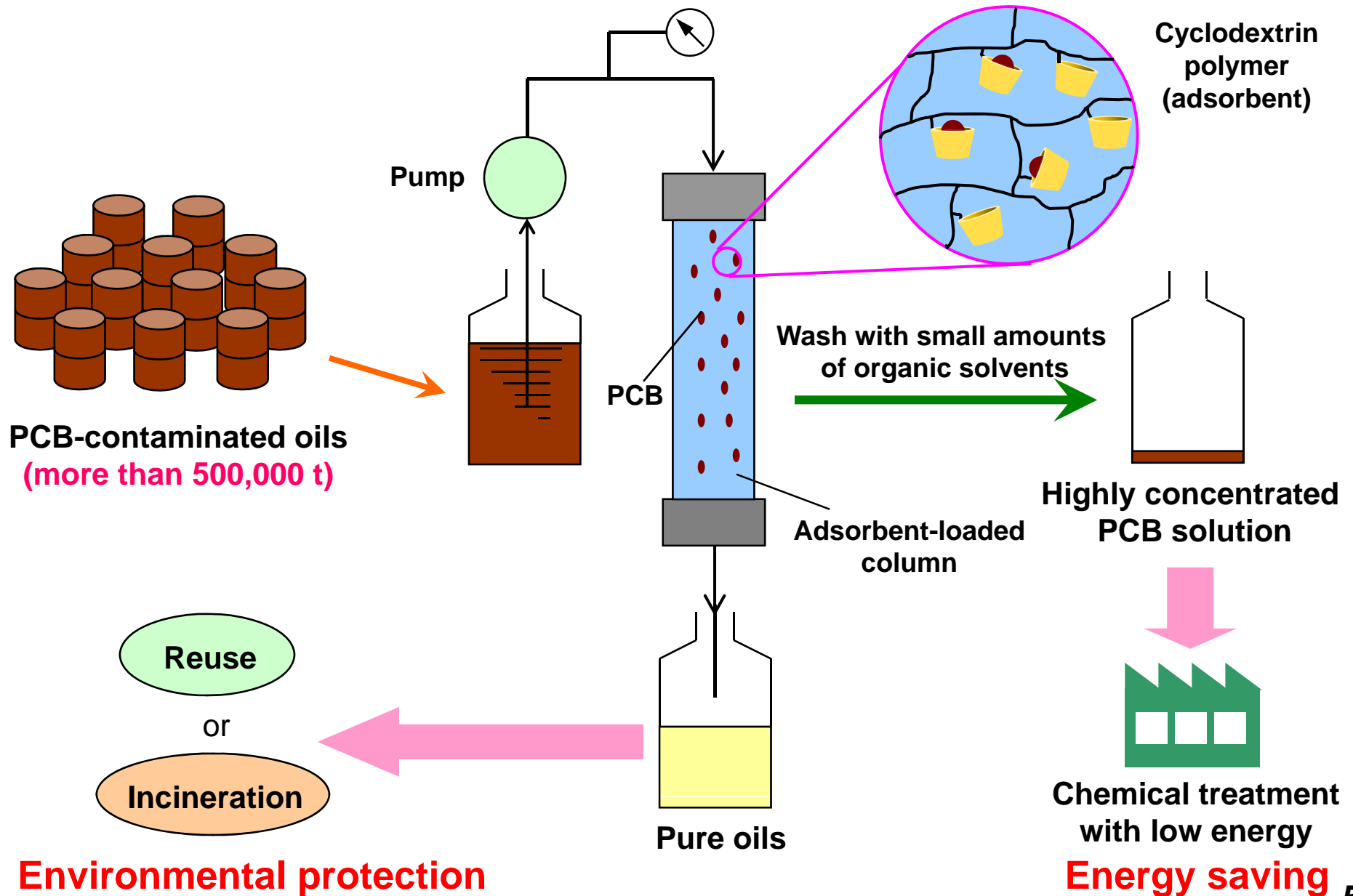
Prolonged reaction times will be required for the treatment of more than 500,000 t of PCB-contaminated oils.

Stockholm Convention on Persistent Organic Pollutants (POPs)

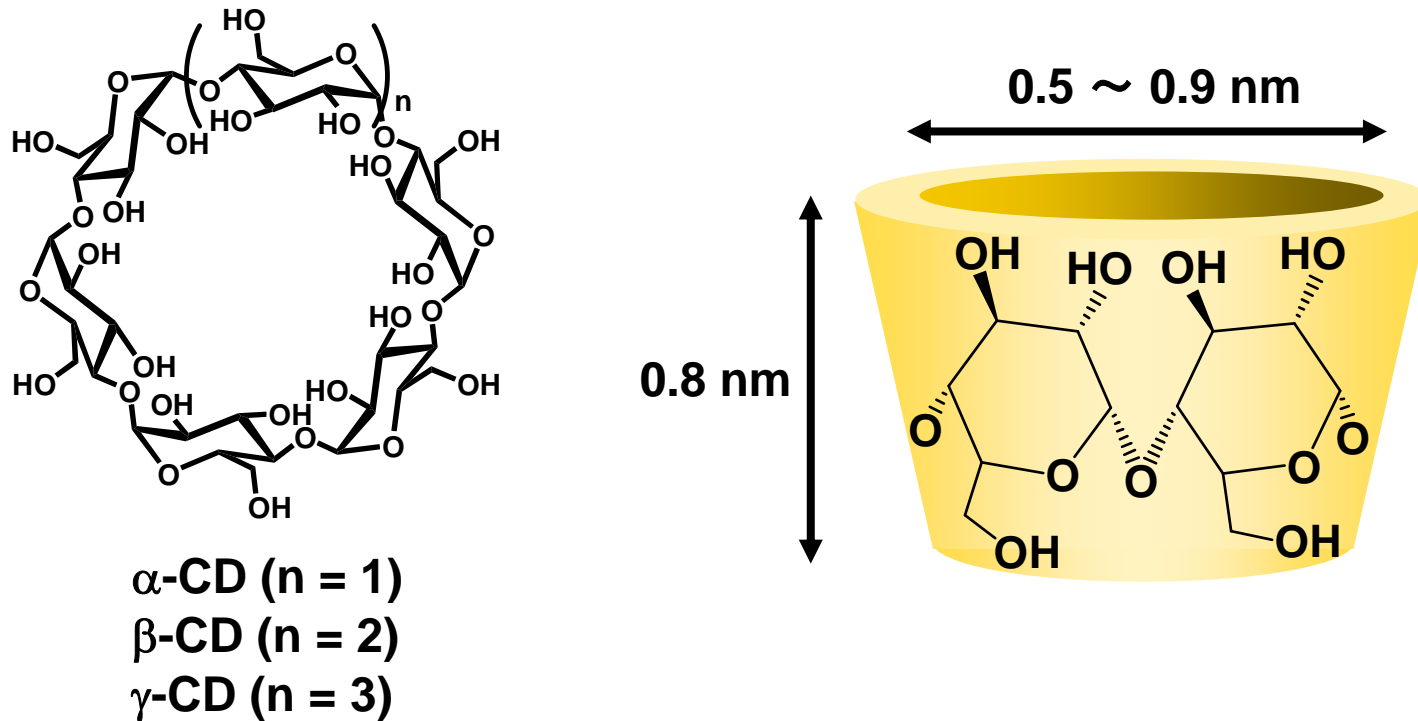
- **Global treaty to protect human health and the environment from chemicals (POPs), including PCBs, that remain intact in the environment for long periods, become widely distributed geographically, and accumulate in the fatty tissue of humans and wildlife.**
- **Adopted in 2001 and entered into force in 2004.**
- **More than 150 countries have agreed to destroy PCBs until 2028.**

Efficient and safe treatment of PCB-contaminated Oils is also a crucial problem from a global viewpoint.

Our Strategy for Treatment of PCB-Contaminated Oils



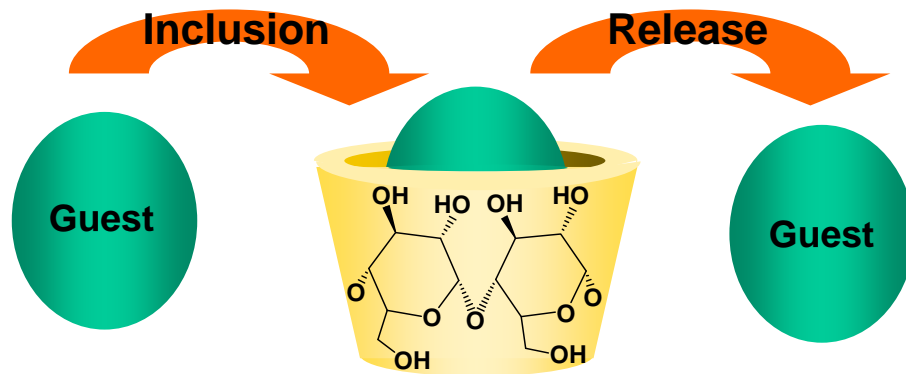
Cyclodextrins (CDs)



- Prepared by transglucosidation of **starch** using a cyclodextrin glucanotransferase (CGTase).
- Have a **hydrophobic cavity** into which an organic compound of an appropriate size and shape can be incorporated (**inclusion**).

Inclusion Complex Formation Using CDs

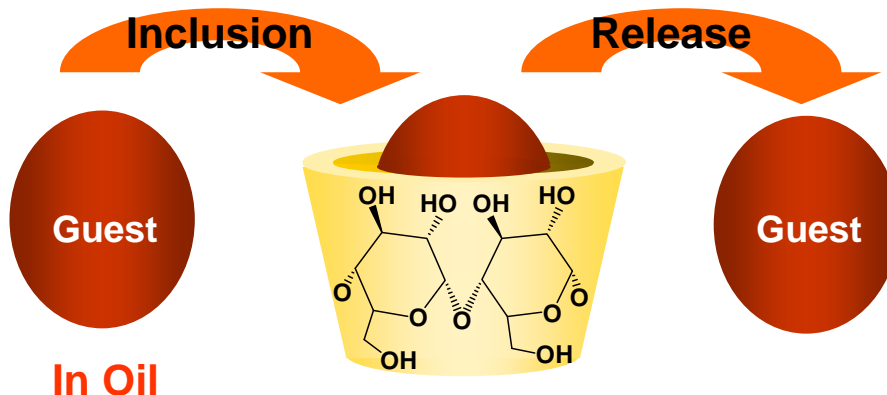
Inclusion Complex Formation with Guest Compounds in Aqueous Media



CD–Guest Inclusion Complex

- Solubilization of Guest Compounds into Water
- Stabilization of Incorporated Guest compounds
- Selective Separation of a Target Compound
- Controlled Release of Incorporated Guest Compounds

Inclusion Complex Formation with Guest Compounds in Oil



In Oil

CD–Guest Inclusion Complex



Removal of 1,2,4-TrCBz from Oil by Si- β -CD

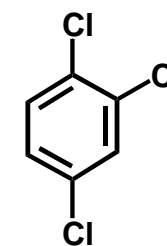
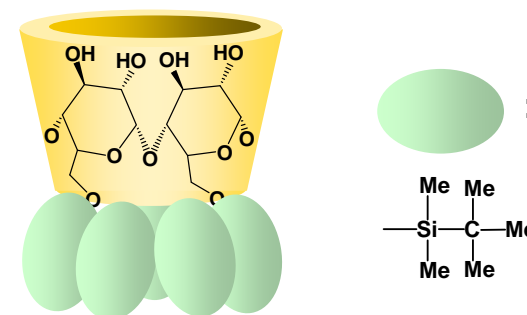
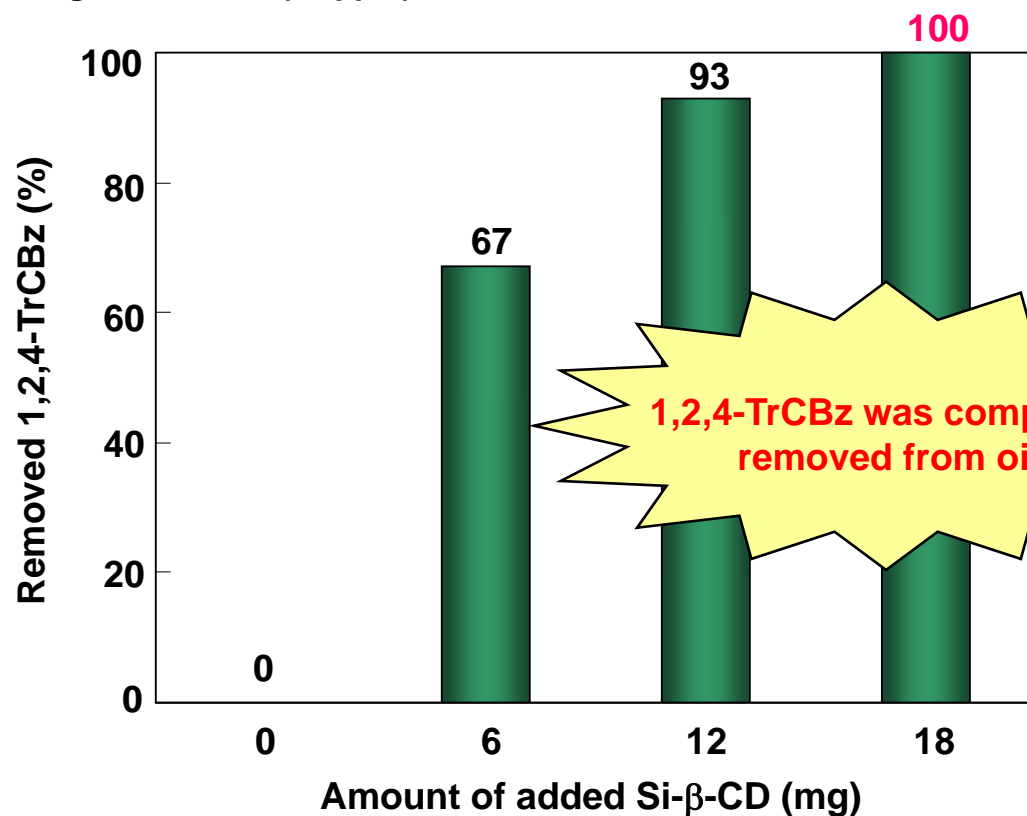
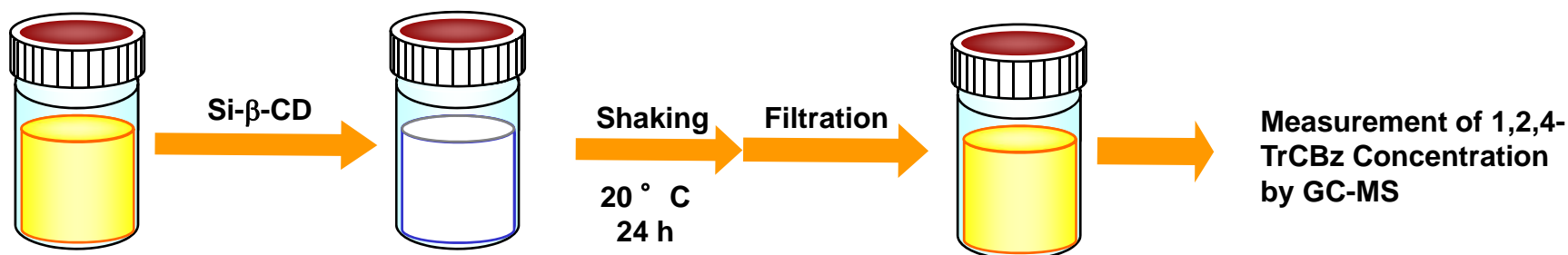
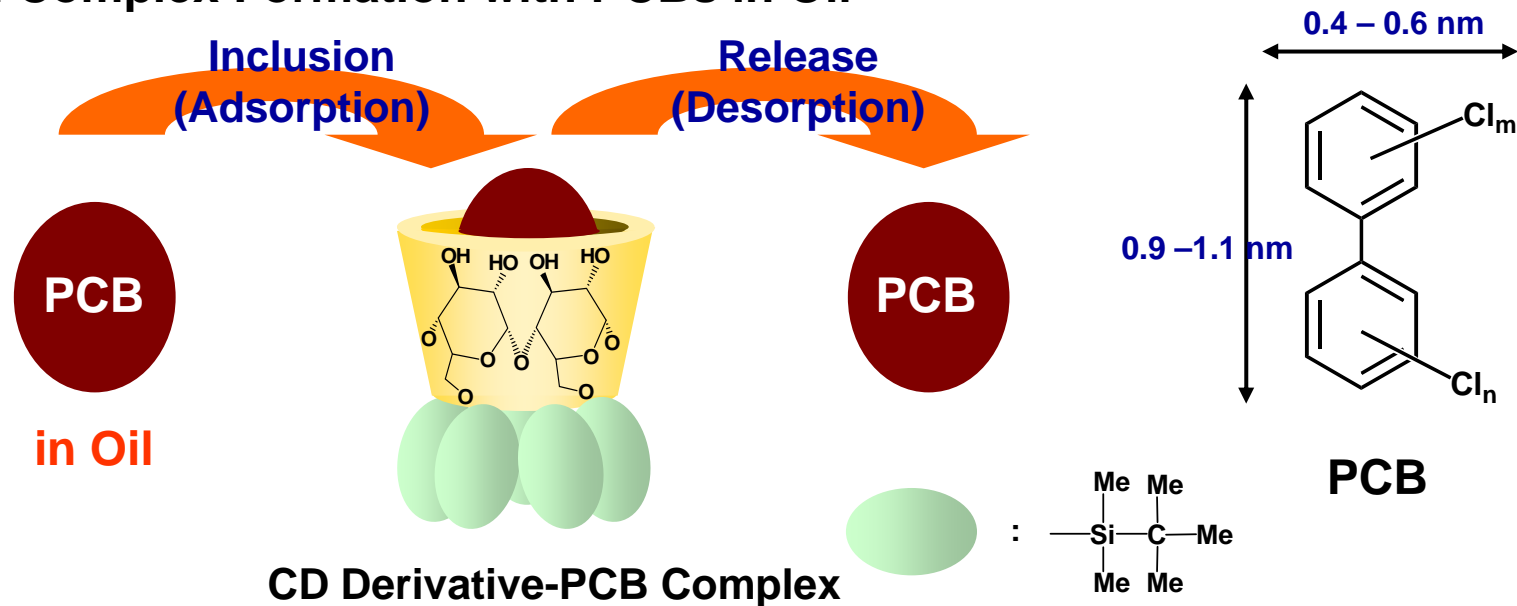


Figure. Relationship between removal percentage of 1,2,4-TrCBz and the amount of added Si- β -CD.

Inclusion Complex Formation between CD Derivatives and PCBs in Oil

Inclusion Complex Formation with PCBs in Oil

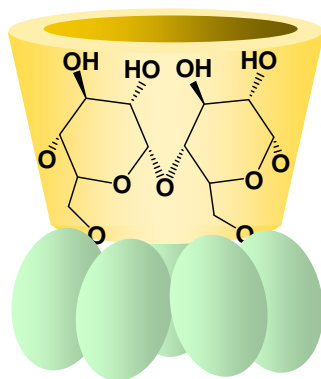


Size and Shape of CD Cavity Suitable for PCBs Inclusion

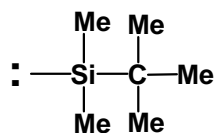
Appropriate Modification of CDs

Selective Removal of PCBs from Oil
Efficient Recovery of Adsorbed PCBs

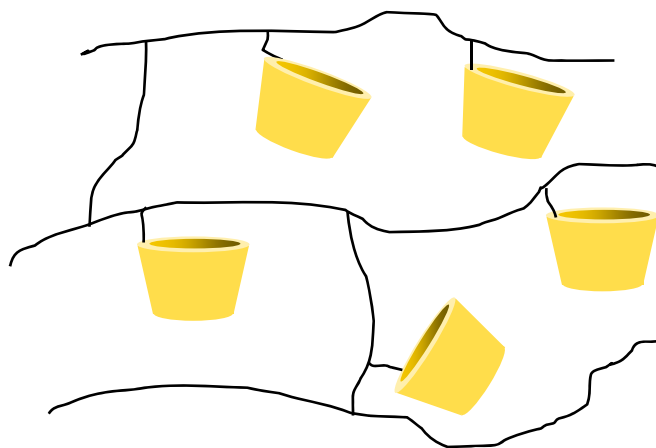
Cyclodextrin Adsorbents Examined



Si-β-CD

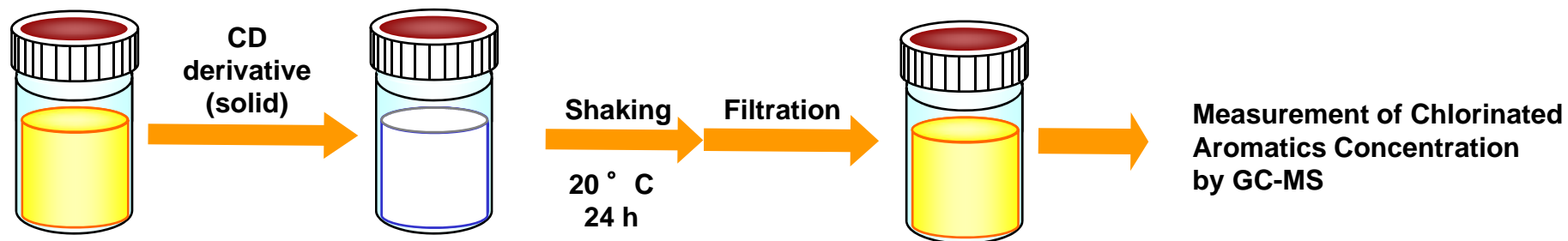


Channel-type γ-CD



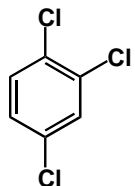
CD polymer

Adsorption Experiments

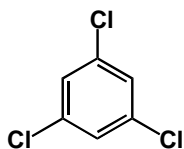


Insulating Oil (300 mg)
Including Chlorinated
Aromatics (90 or 100 ppm)

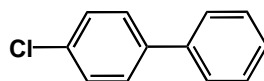
Chlorinated Aromatic Compounds



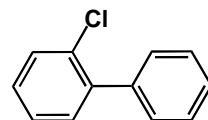
1,2,4-TCBz



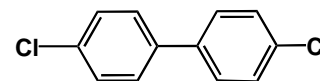
1,3,5-TCBz



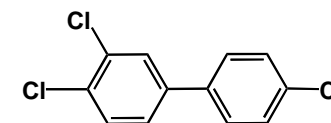
4-MCB



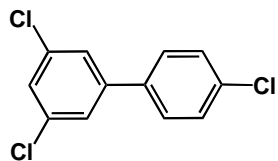
2-MCB



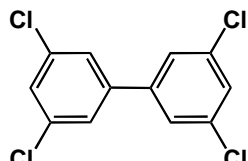
4,4'-DCB



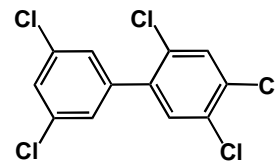
3,4,4'-TrCB



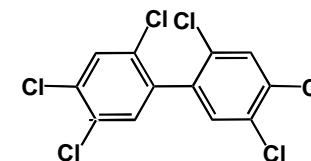
3,4',5-TrCB



3,3',5,5'-TeCB

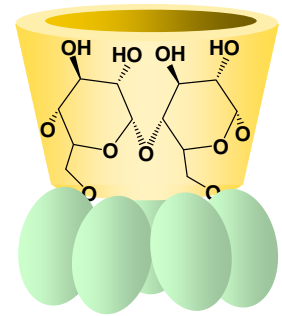
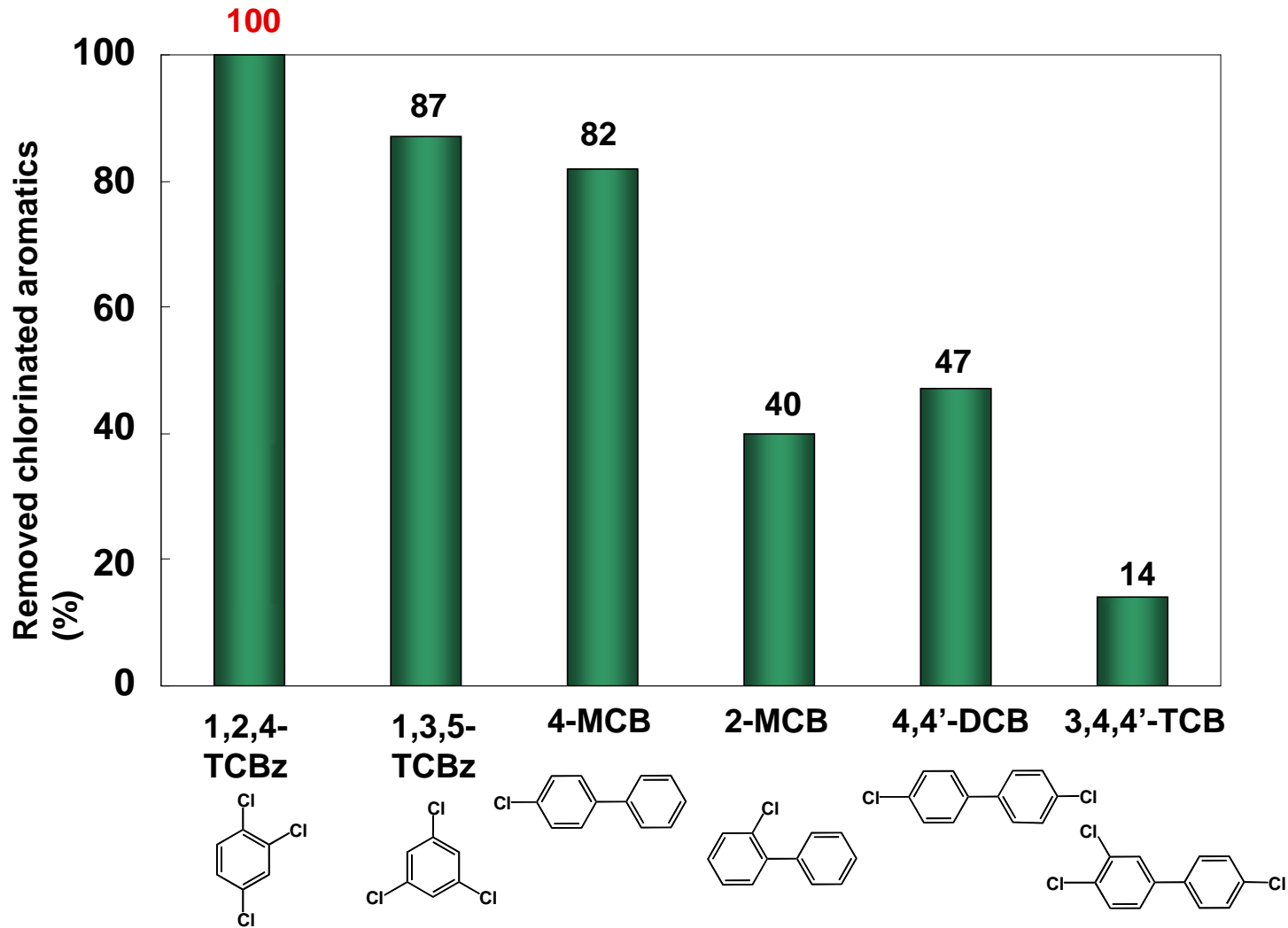


2',3,4',5,5'-PeCB

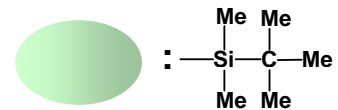


2',2',4,4',5,5'-HeCB

Removal of Chlorinated Aromatics from Insulating Oil by Si- β -CD

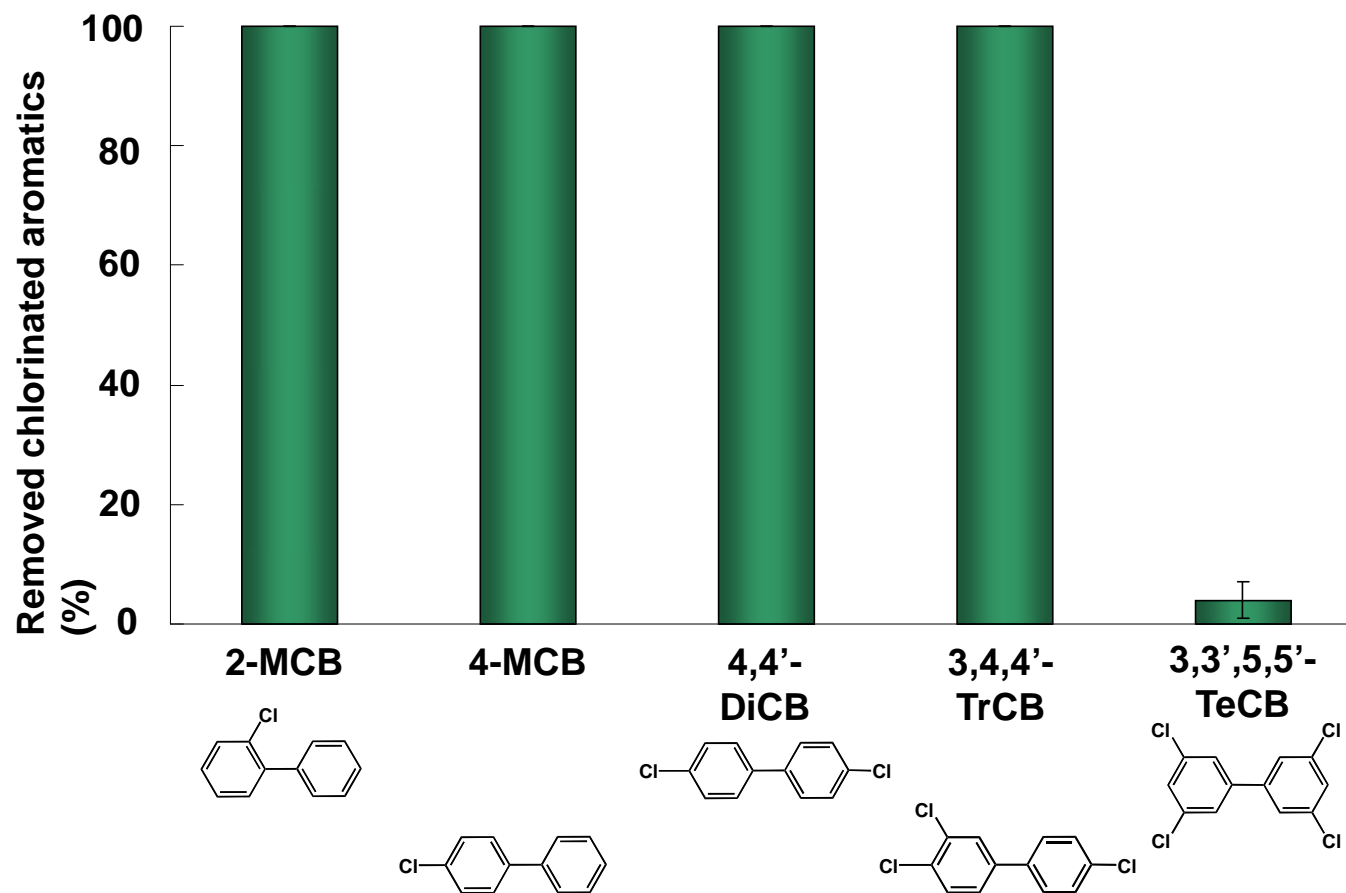


Si- β -CD



Initial concentration of chlorinated aromatics: 90 ppm (in 240 mg of insulating oil)
Si- β -CD: 20 mg

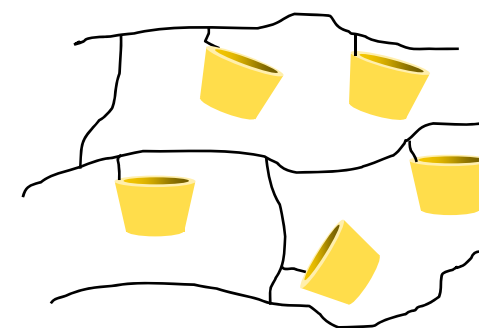
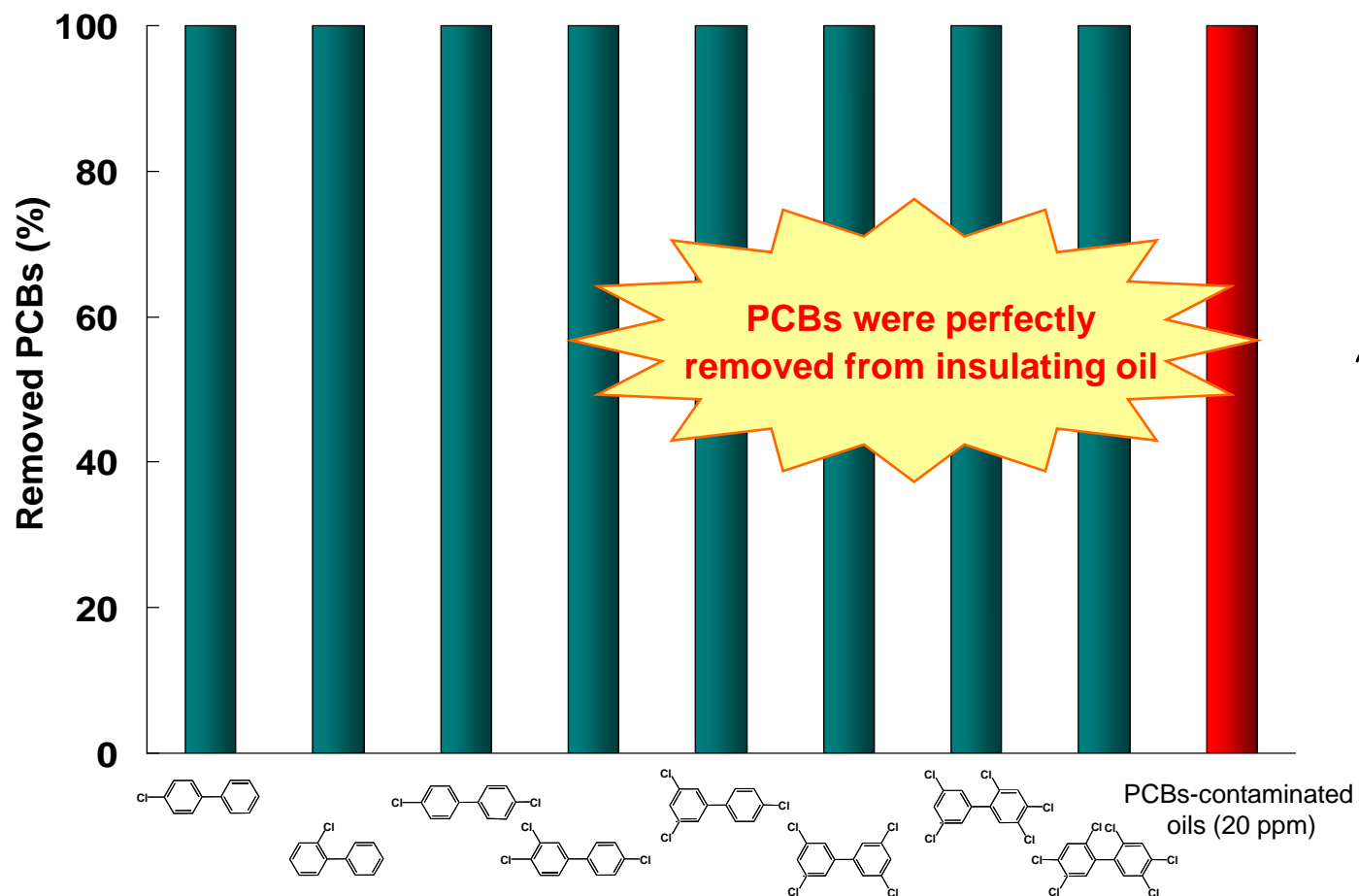
Removal of Chlorinated Aromatics from Insulating Oil by Channel-type γ -CD



Channel-type γ -CD

Initial concentration of chlorinated aromatics: 100 ppm (in 300 mg of insulating oil)
Channel-type γ -CD: 180 mg

Removal of PCBs from Insulating Oil by CD Polymer



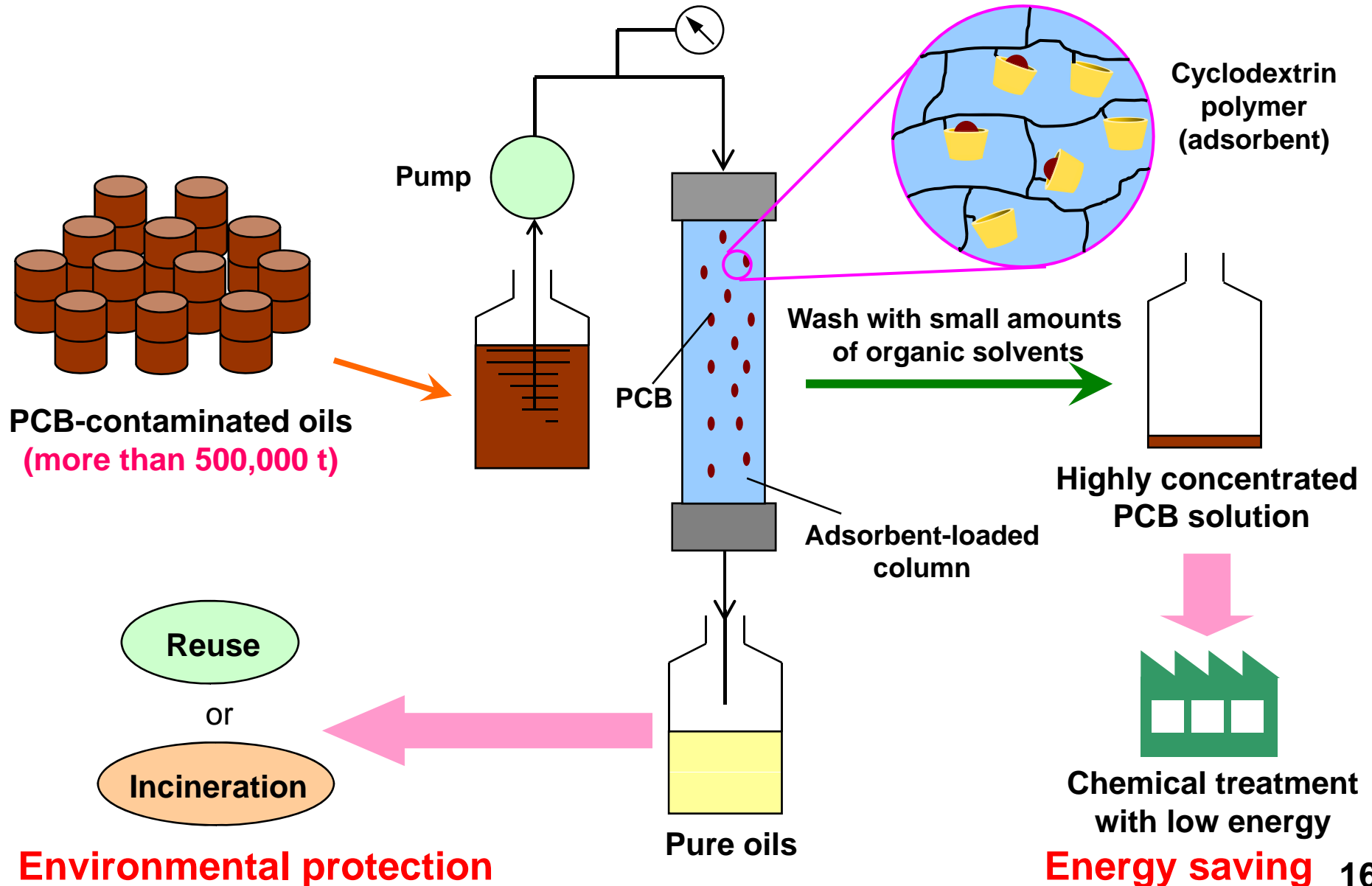
CD polymer (adsorbent)

Initial concentration of PCB: 100 ppm (in 400 mg of insulating oil)
Amount of CD polymer: 200 mg

Photograph of CD Adsorbent and Column



Quick and Energy-Saving Treatment of PCB-Contaminated Oils



Conclusions

- We developed **cyclodextrin adsorbents** that were highly useful for the removal and recovery of polychlorinated biphenyls (PCBs) from oils.
- By passing PCBs-contaminated oils through a column of the cyclodextrin adsorbent, **the efficient and complete removal of PCBs from oils** is accomplished.



This technique for PCBs removal and recovery will contribute to **the quick and energy-saving treatment of large amounts of PCBs-contaminated oils** that are kept in many countries, including Japan.

We are now working toward practical use of this technique with NEOS Company, Ltd. (supported by Japan Science and Technology Agency, JST).

Acknowledgments

Osaka University

Assoc. Prof. Toshiyuki Kida
Mr. Yoshinori Fujino

NEOS Company, Ltd.

Dr. Eiichi Kato,
Dr. Kazuhiro Miyawaki

Funds:

- A Grant for Promotion of Environmental Technology and Development from the Ministry of the Environment of Japan (2007)
- A Fund for Technology Development from Japan Science and Technology Agency (JST) (2008–2013)