APPLICATION OF EXTRACTION TECHNOLOGY USING LIQUID DIMETHYL ETHER TO PCBS FROM RIVER SEDIMENT

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Introduction

River and harbor sediments are sometimes severely contaminated with PCBs that originate from illegally dumped devices such as electric condensers and transformers. There are many contaminated sites throughout the world. It is necessary to remove PCBs from these sediments in order to reduce health risks to humans and ecosystems. Given the large volume and high water content of river and harbor sediments, a removal process must be efficient and economical. Solvent extraction technology is one method for removing PCBs from contaminated soil and sediments[1]. This technology has some advantages such as relatively low energy consumption compared with thermal treatment. However, to recover and reuse the solvent after the extraction treatment, advanced heating devices are needed to separate (by evaporation) and refine the solvent from the mixture of solvent and water[2, 3]. Thus, this technology is complicated and ultimately consumes a large amount of energy.

In the present study, we focus on using liquefied dimethyl ether (DME) as an extractant for the solvent extraction of PCBs from sediments. Solvent extraction using liquefied DME, a simple organic compound, to treat sediment has many potential advantages. First, it achieves high efficiencies for the removal of organic contaminants and water, as 7 g of water are soluble in 100 g of liquefied DME. Second, DME easily undergoes a phase transition[4]. Although a gas at room temperature under atmospheric pressure, DME is liquefied at room temperature under pressures of 0.5–0.6 MPa. Therefore, after an extraction is performed, the pressure can be reduced to less than 0.5 MPa to allow the gaseous DME to be easily separated from the target compounds. Subsequently, the gaseous DME can be liquefied by increasing the pressure, so that the DME can be reused without significant loss. Figure 1 shows the concept of the DME extraction of PCBs from river sediments. This study evaluated the extraction characteristics of PCBs from contaminated sediments by using a DME flow-type experimental apparatus.
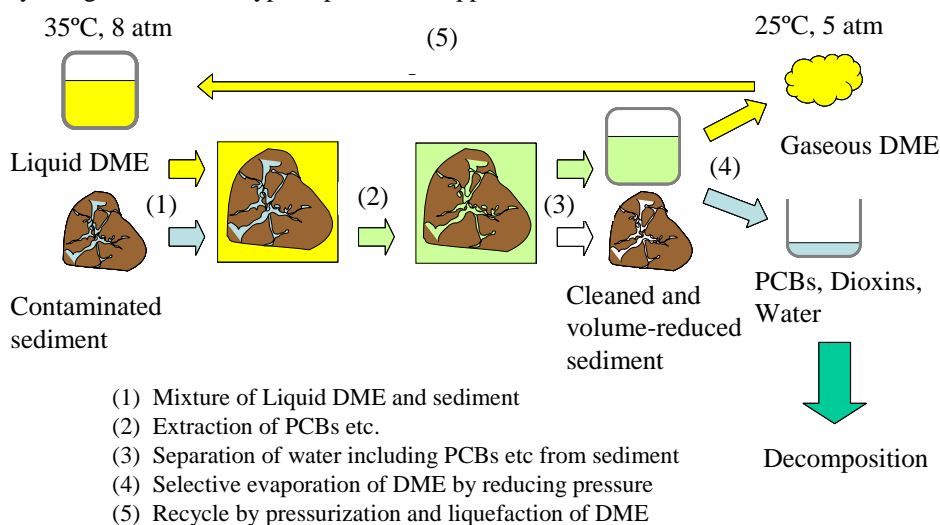

(1) Mixture of Liquid DME and sediment
(2) Extraction of PCBs etc.
(3) Separation of water including PCBs etc from sediment
(4) Selective evaporation of DME by reducing pressure
(5) Recycle by pressurization and liquefaction of DME

Figure1 Concept of DME extraction of PCBs in river sediment.

Materials and Methods

River sediment was sampled at the Shorenji River bed, around Okijima Bridge in Osaka City using a core sampler in the vertical depth direction. In this study, the sediment at a depth of 5 m was used for the experiment.

The schematic flow of a DME flow-type experimental apparatus is shown in Fig.1. It is composed of three parts: a filling vessel for liquid DME (TVS-1-100; Taiatsu Techno Corp.), an extraction vessel (HPG-10-5; Taiatsu Techno Corp.), and a storage vessel for separated liquid (HPG-96-3; Taiatsu Techno Corp.). First, a sediment ball (diameter, 4 mm), which had a water content of 60.4%, was made from the sediment sample. Then, 1 g from sediment balls was packed into the extraction vessel. Liquid DME was added to the filling vessel by cooling gaseous DME

Activated carbon column

Filling vessel for liquid DME   Extraction vessel   Storage vessel for separating liquid

Figure 2 The schematic flow of a DME flow-type experimental apparatus.

(Pure4.8LP; Sumitomo Seika Chemicals Co., Ltd.) with ethanol and ice. Under set conditions and using nitrogen gas flow from a gas cylinder, the liquid DME was then passed into the extraction vessel that contained the sediment samples. The separated liquid entered the storage vessel. The DME was separated from the water and PCBs by reducing the pressure to ambient pressure, changing the liquid DME to gaseous DME. The vaporized DME was passed through a column containing 5.5 g of granular activated carbon (Shirasagi C2C, 20-48 mesh; Takeda Pharmaceutical Co., Ltd.) for 1 h, to trap trace gaseous PCBs.
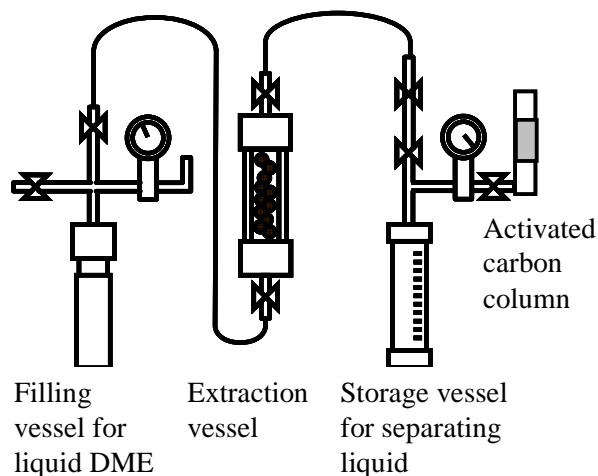
The analysis of PCBs in the sediment before and after extraction was based on the official method for sediments used by the Ministry of Environment[5]. The sediments were heated with a solution of 1 M KOH in ethanol at 80°C for 1 h. After cooling, the PCBs were extracted by hexane. The separated liquid was liquid-liquid extracted by hexane, and the activated carbon was soxhlet extracted by toluene. After clean-up, the concentrations of the PCBs as listed in Table 1 were measured by high-resolution gas chromatography/low- resolution mass spectrometry (HRGC/LRMS; (HP6890/5973; Agilent) with a HP-5MS column). The total concentration of PCBs in the sediment was 8.70 mg/kg-dry (Table 1).

Table 1 PCBs concentration in the sediment (unit: mg/kg-dry).

DiCBs	0.413
TriCBs	1.79
TeCBs	2.94
PeCBs	1.97
HxCBs	0.975
HpCBs	0.326
OcCBs	0.262
NCBs	0.0286
DeCB	0.00
PCBs (total)	8.70

Results and Discussion:

The effect of passing velocity of liquid DME

The change of water content and PCBs concentrations in the sediment at a liquid/solid ratio of 60mL/g in the range of velocity of liquid DME from 0.132 to 1.584mm/sec is shown in Fig.3. As the velocity of liquid DME increases, the water content and PCBs concentration significantly decrease. The lowest water content with 5.26% was obtained at the
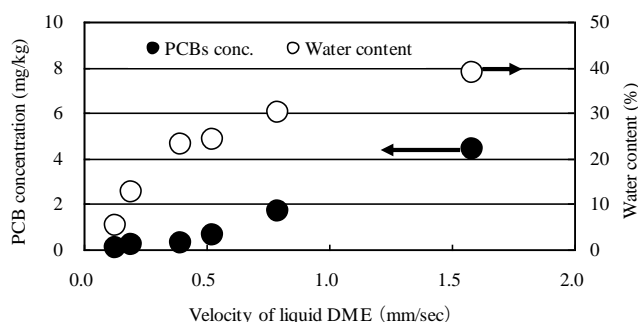

Figure 3 The change of water content and PCBs concentrations in the sediment at a liquid/solid ratio of 60mL/g in the range of velocity of liquid DME from 0.132 to 1.584mm/sec.

velocity of 0.132 mm/sec, which means that the 96.4% of water in the sediment was dewatered. As for PCBs, the same condition gave the lowest concentration with 0.10mg/kg-dry, which indicates the 98.8% of PCBs was removed. This is reason why lower velocity of liquid DME causes the increase of contact time between sediment and liquid DME.

The effect of liquid/solid ratio

Figure 4 shows the changes in the water content and PCB concentration removed from the sediment at a liquid DME velocity of 0.792 mm/s as the liquid/solid ratio was changed from 30 to 180 mL/g. The water content and PCB concentration decreased substantially with an increase in the liquid/solid ratio. Both the lowest water content (4.90%) and the lowest PCB concentration (0.075 mg/kg-dry), indicating the removal of 96.6% of the water and 99.1% of the PCBs from the sediment, were obtained at the liquid/solid ratio of 180 mL/g. However, increasing the amount of liquid DME passing through the sediment
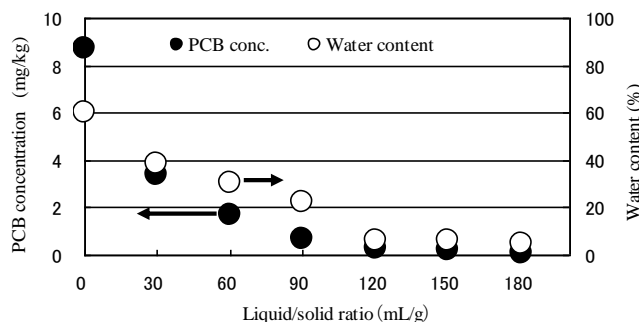

Figure 4 The change of water content and PCBs concentrations in the sediment at a velocity of liquid DME of 0.792mm/sec in the range of liquid/solid ratio from 30 to 180mL/g.

required more power from the liquid DME supply pump. An effective extraction could be performed with a smaller amount of DME by lowering the velocity of the liquid DME, although this would require more time or a larger extraction vessel.

The mass balance of water and PCBs

The mass balance of water and PCBs under two experimental conditions; (1) DME extraction with the velocity of 0.132mm/sec at liquid/solid ratio of 60mL/g and (2) DME extraction with the velocity of 0.792mm/sec at liquid/solid ratio of 180mL/g was investigated. The results are shown in Fig.5 In both water and PCBs, the mass before extraction experiment is good agreement with the summation of mass in the sediment, separate liquid and activated carbon. 0.088-0.095ug of PCBs was found in activated carbon, which means that 2-3% to original PCBs in the sediment moves to gaseous phase. If we reuse the DME by liquefying repetitively, it is thought that it is necessary to refine the DME after extraction by activated carbon etc..
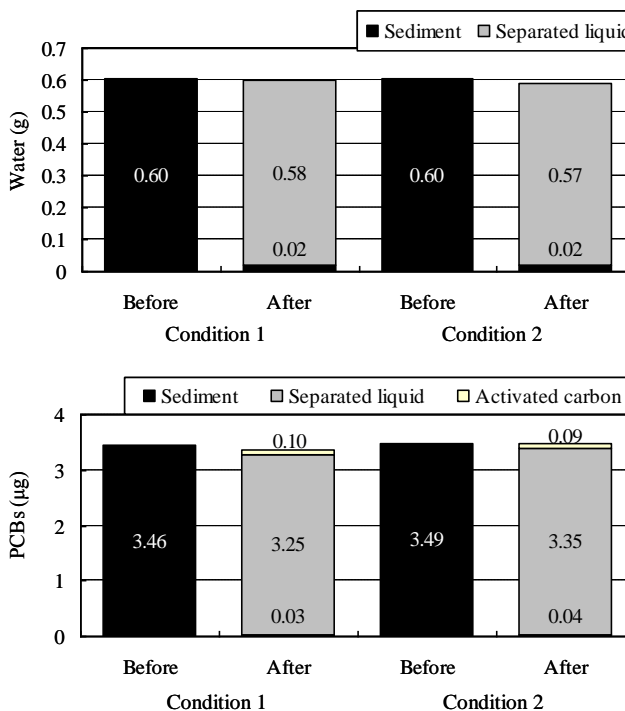
The extraction rate of PCBs

According to Fig. 4, the PCB concentration in the sediment was reduced substantially as the liquid/solid ratio increased. The liquid/solid ratio was converted to extraction time, and the relationship between the extraction time and the logarithm of Ct/C0,

Figure 5 The mass balance of water and PCBs in DME extraction experiment (upper case: water, lower case: PCBs).

(where Ct is the PCB concentration in the sediment at t seconds after the extraction and C0 is the PCB

concentration in the original sediment) was determined. The relationship was discovered to be linear, suggesting that the extraction has a first order reaction rate. Table 2 shows the slope of the regression line, the constant of the extraction rate (k), and the correlation coefficient (R).

The relationship is linear, which suggests that the extraction rate is expressed by the first order reaction rate. Table 2 shows the slope of regression line; constant of extraction rate (k), and correlation coefficient(R). The constant of extraction rate intend to be high in higher chlorinated compounds, which indicates that it is easy to extract higher chlorinated compounds. Etoh et al., reported that the removal of higher chlorinated compounds tend to be high in PCBs extraction from contaminated soil using isopropanol[6]. This fact is agreement with our results. This may be reason why higher chlorinated compounds have high hydrohobicity and lipophilicity.

Table 2 The constant of extraction rate (k) and correlation coefficient (R).

	k (1/sec)	R^2
DiCBs	0.00145	0.972
TriCBs	0.00214	0.971
TeCBs	0.00210	0.980
PeCBs	0.00224	0.957
HxCBs	0.00225	0.972
PCBs (total)	0.00210	0.985

In this study, we showed that DME extraction achieved the effective and simultaneous removal of water and PCBs. Previous studies using DME to remove water from sewage sludge and brown coal with high water content have estimated that the energy consumption via this technology is half of that for a conventional dryer. We plan to investigate the energy consumption and safety of this technology after optimizing the operating parameters.

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