LABORATORY-SCALE EXAMINATION OF THE DECHLORINATION OF SHORT-CHAIN CHLORINATED PARAFFINS USING THE METAL SODIUM DISPERSION METHOD

Fujimori T[1], Ogura M[2], Takaoka M[1]

[1]Kyoto University, Kyoto, Japan, 615-8540, fujimori.takashi.3e@kyoto-u.ac.jp; [2] Kobelco Eco-Solutions Co., Ltd., Kobe, Japan, 651-2241

Introduction

The metal sodium (Na) dispersion method is a technique used for the dechlorination and detoxification of chlorinated organic compounds, and involves mixing fine particles of metal Na into oil. Metal Na dispersion can destroy polychlorinated biphenyls (PCBs) and is categorized as an alkali metal reduction method in the general technical guidelines produced by the Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal[1]. Using this technique, a destruction efficiency (DE) of more than 99.999% and destruction removal efficiency (DRE) of 99.9999% have been reported for PCBs and certain pesticides (chlordane and hexachlorocyclohexane (HCH)) by the Ministry of the Environment, Japan (2004)[1]. The metal Na dispersion method has therefore been officially recommended to reduce PCBs in waste, as required by the "Act on Special Measures concerning the Promotion of the Proper Treatment of PCB Wastes" (2001) in Japan[2]. Commercial treatment plants applying metal Na dispersion to destroy PCBs in waste are operating in an official capacity in Japan[2]. Although short-chain chlorinated paraffins (SCCPs) have been used as a lubricant in metal working fluids, and as flame retardants in plastics, they are listed in Annex A (Elimination) of the Stockholm Convention on persistent organic pollutants (POPs), and products containing SCCPs require detoxification. SCCPs have viscous and oily characteristics, which are similar to those of PCBs used as insulation oil. This suggests that detoxification of SCCPs could be possible using the metal Na dispersion method[3]. The "SP method" was developed as one possible metal Na dispersion method and has the advantage of inhibiting polymerization byproducts during the reaction process through the addition of hydrogen donors; it can also operate at low temperatures[4,5]. In this study, we applied the SP method to a wax sample containing SCCPs to assess the treatment effect.

Materials and methods

A wax sample (52#; Shandong Yousuo Chemical Technology Co., Ltd., China) containing chlorinated paraffins was used as the substrate. Total SCCPs (ΣSCCPs), which consisted of molecules with a carbon number from 10 to 13 (C_{10} – C_{13}) and chlorine number from 5 to 9 (Cl_5 – Cl_9), were found to account for 58 wt% of the wax sample following an instrumental analysis.

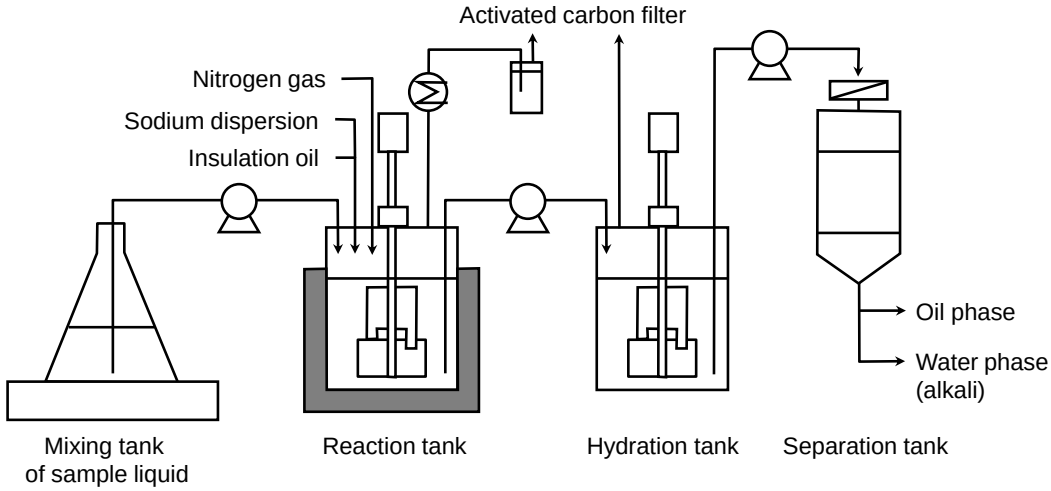

Figure 1: Laboratory-scale reaction apparatus for operating the SP method using a 2-L reaction tank.

A 2-L reaction vessel (1,800 (width) × 600 (depth) × 1,000 cm (height) was used as the apparatus in which the SP method was conducted, as shown in **Figure 1**. This apparatus comprised a 2-L separable flask, mantle heater (1.2 kW), stirrer, pump to deliver solution, temperature controller, exhaust gas condenser, activated carbon filter to treat the exhaust gas, and an oxygen meter. We used a metal Na dispersion (SD30; Kobelco Eco-Solutions Co., Ltd.), isopropyl alcohol (IPA) as a hydrogen donor, ion-exchange water as a salt extraction agent,

and insulation oil (transformer oil H; Idemitsu Kosan Co., Ltd.) as the diluting solvent. The wax sample, insulation oil, and IPA were mixed by stirring in a mixing tank to create a sample liquid, as shown in **Figure 2A**. The Na dispersion and insulation oil (for controlling the liquid volume) were stirred at room temperature under nitrogen gas in a reaction tank, as shown in **Figure 2B**. The sample liquid was supplied to the reaction tank, which was kept at the reaction temperature for 3 h, as shown in **Figure 2C**. An aliquot of the liquid in the reaction tank was collected and used for quantification of SCCPs by instrumental analysis. The liquid was transferred to a hydration tank for the extraction of salts into the water phase, by dechlorination to inactivate residual Na (**Figure 2D**). The hydration liquid was moved to the separatory funnel and the oil and water phases were collected after adequate separation by being allowed to stand for more than 8 h (**Figure 2E**).

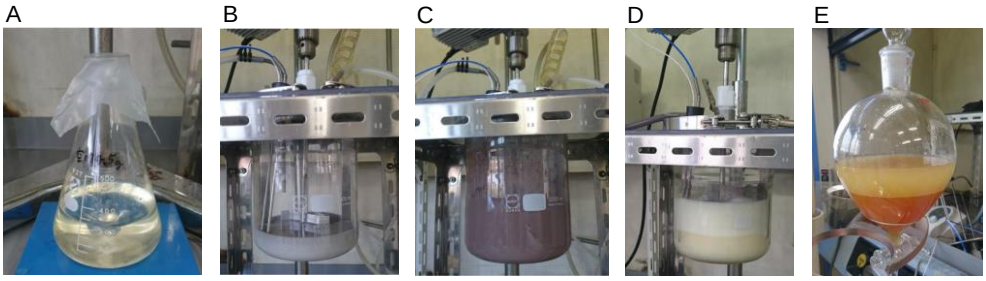

Figure 2: Representative photographs of the SP method applied to the wax containing short-chain chlorinated paraffins (SCCPs). (A) Sample liquid containing the wax, insulation oil, and isopropyl alcohol (IPA) in the mixing tank. (B) Preparation of the sodium (Na) dispersion and insulation oil in the reaction tank. (C) General state in the reaction tank after beginning to operate the SP method. (D) Extraction of salts into the water phase in the hydration tank. (E) Upper oil phase and lower water phase in the separation tank.

We added water to the aliquot of liquid collected from the reaction tank to inactivate and hydrate excess Na. The hydration liquid was centrifuged for 5 minutes. Then, 10 mL of hexane was added to 600 µL of the oil phase for dilution, following which 10 mL of sulfuric acid was added and shaken. The solution was left to stand and finish separating, with the hexane phase used for instrumental analysis. Although there have been many studies of methods that could potentially quantify SCCPs, in this study, we used a gas chromatograph equipped with an electron capture detector (GC-µECD; 6890N; Agilent Technology, Inc., USA) for the preliminary measurement of SCCPs. The measurement method using the GC-µECD proceeded as follows. An SPB-TM5 column (30 m, 320-µm inside diameter, 0.25-µm thickness) was used as the capillary column. Helium and nitrogen were used as the carrier and make-up gases, respectively. The inlet zone was kept at 250˚C in the splitless mode. The injection volume was 2 µL. The heating program of the column was set as 60˚C → 10˚C/min → 140˚C → 1˚C/min → 210˚C → 3 C/min → 260˚C. The temperature of the detector was kept at 320˚C.

Results and discussion

We determined the limit of quantification (LOQ) of ΣSCCPs using the GC-µECD. The wax sample was diluted to 6.6 mg/kg by insulation oil, and ΣSCCPs were then measured five times in the same diluted sample. Ten times the standard deviation of this measurement was 2.3 mg/kg, which was accepted as the LOQ of ΣSCCPs in this study.

A total of six experiments were run under various conditions, including changes to the initial amounts of wax and Na dispersion, as shown in **Table 1**. The ΣSCCP concentration was lower than the LOQ after 30 minutes of reaction, under all conditions. The DE of ΣSCCPs was calculated by subtracting the residual amount of ΣSCCPs in the solution in the reaction tank from the initial amount of ΣSCCPs in the wax. As a result, we could determine the DE of the SCCPs by the SP method. The DE of ΣSCCPs was over 99.99% after 10 minutes of reaction under several conditions, in which the initial concentrations in the wax ranged from 5 to 30% (runs 2 – 6) as shown in **Table 1**.

In In contrast, at the minimum initial concentration in the wax (i.e., 1%), the DE was about 81% at 10 minutes and over 99.97% after 60 minutes, which was lower than under other conditions. These conditions (run 1) were set to determine the temperature range over which adequate

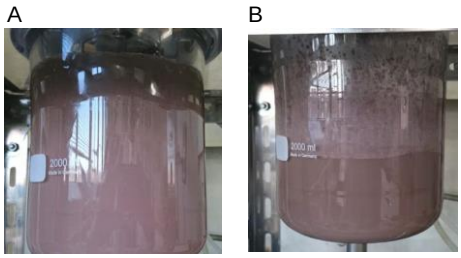

Figure 3: Bubble release in the reaction tank. (A) Commencement of the supply of the liquid sample. (B) Stable condition after bubble release was completed.

dechlorination of SCCPs could be achieved. The temperature in the reaction tank was 30˚C at 10 minutes, after which the color of the liquid in the reaction tank did not change from the grayish white of the Na dispersion (see **Figure 2B**). Therefore, a substantial dechlorination could not be achieved at this temperature. The reaction liquid was a red color when the temperature was increased to 60–90˚C, as shown in **Figure 2C**. A change in the reaction liquid to a red color is a general sign that dechlorination is occurring when this technique is used for PCB destruction. Therefore, a temperature of 30˚C was not sufficient to promote dichlorination. The dechlorination of SCCPs required a temperature of over 60˚C to be maintained for about 1 h.

We assessed the influence of the initial ΣSCCP concentration in the wax through runs 2–6. For a liquid sample in the reaction tank containing an initial ΣSCCP concentration of 5–30% in the wax, the temperature of the reaction liquid was increased to 90˚C by the heat of reaction. The temperature of the reaction tank was kept at 90˚C by controlling the amount of liquid sample. Bubble release of reaction liquid was used to supply the liquid sample in runs 2–6 (**Figure 3A**). A bubble phase with the same height as the liquid phase in the reaction tank was observed. Therefore, the stirring speed was set to 300 rpm to disperse the bubbles and ensure that the reaction liquid was mobilized. The ΣSCCP concentration under each condition was below the LOQ (2.3 mg/kg) in the reaction liquid at 10, 30, 60, 120, and 180 minutes.

Table 1: Experimental conditions and destruction efficiency (DE) of ΣSCCPs by the SP method for each run.

Run			1	2	3	4	5	6
Initial concentration of the wax containing SCCPs[a]		(%)	1	5	10	10	20	30
Reaction temperature		(˚C)	30～90[c]	90	90	90	90	90
Initial amount of the wax containing SCCPs		(g)	5.0	20.0	40.1	40.2	48.0	51
Amount of diluting solvent (insulation oil)		(g)	496.5	380.3	360.0	360.3	192.6	119.1
Amount of Na dispersion		(g)	21.9	77.2	176.2	207.1	247.8	263.3
Amount of isopropyl alcohol (IPA)		(g)	5.0	24.4	38.2	38.6	46.4	49
Destruction efficiency of ΣSCCPs at each reaction time[b]	10min	(%)	-	>99.994	>99.996	>99.996	>99.997	>99.997
	30min		80.967	>99.994	>99.996	>99.996	>99.997	>99.997
	60min		>99.976	>99.994	>99.996	>99.996	>99.997	>99.997
	90min		>99.976	-	-	-	-	-
	120min		-	>99.994	>99.996	>99.996	>99.997	>99.997
	180min		-	>99.994	>99.996	>99.996	>99.997	>99.997

[a] Initial amount of the wax/(initial amount of the wax + amount of diluting solvent) × 100

[b] (Initial amount of ΣSCCPs - amount of ΣSCCPs in reaction solution)/Initial amount of ΣSCCPs × 100, 58% was used as concentration of ΣSCCPs.

[c] Temperature was different at each reaction time: About 30˚C after 10 min, about 50˚C after 30 min, about 60˚C after 60 min, about 90˚C after 90 min

By cooling the reaction liquid after each run to room temperature, the reacted liquid was hydrated and extracted. Finally, the oil and water phases were separated as shown in **Figure 2E**. The water phase had alkaline properties and its pH was nearly 14. A brown solid material was observed at the oil-water interface, but it was difficult to collect because only trace amounts were present. Previously, similar trace amounts of a solid material were found when applying the SP method to PCB treatment, and we identified it as a polymerized compound with a biphenyl structure. Therefore, it was likely that the brown solid material was an aliphatic polymer, which was a byproduct of the application of the SP method to SCCPs. GC-μECD revealed 30 mg/kg of ΣSCCPs in oil samples collected from the separation tank in run 2. One reason for this might be contamination of the hydration process by unreacted SCCPs on the upper inner wall of a reaction tank, due to bubble release as the liquid sample was supplied into the mixing tank, as shown in **Figure 3B**.

The metal Na dispersion method applied to PCBs was classically derived from an interconversion reaction between Na and aromatic compounds[6,7]. Considering the dechlorination reaction of PCBs by metal Na dispersion[8,9], similar dechlorination and hydration might occur in the case of SCCPs through the following reactions:

$$\text{R-Cl} + 2\text{Na} \rightarrow \text{R-Na} + \text{NaCl} \qquad \text{(R1)},$$

$$\text{R-Na} + \text{H}_2\text{O} \rightarrow \text{R-H} + \text{NaOH} \qquad \text{(R2)},$$

where R is an aliphatic carbon in an SCCP structure. Because the red color of the reacted liquid vanished in the hydration tank (**Figure 2D**), it might have been derived mainly from R-Na products in reaction (R1). The alkaline properties in the water phase in the separation tank supported the formation of sodium hydroxide (NaOH) via reaction (R2). After the dechlorination of SCCPs, the final products in the oil phase were estimated to be short-chain paraffins without chlorines. However, the detailed reaction path and byproducts from this system applied to SCCPs need to be studied in the future.

Conclusions

We applied a metal Na dispersion method (the SP method) to a wax sample containing SCCPs. Effective dechlorination of the SCCPs was confirmed using laboratory-scale reaction apparatus, as shown in **Figure 1**. The DE of ΣSCCPs was over 99.99% after 10 minutes of reaction at 90˚C under several conditions, in which the initial ΣSCCP concentration of the wax ranged from 5 to 30% (**Table 1**). The optimal treatment conditions, i.e., the initial concentration of wax containing SCCPs, reaction temperature, and reaction time, will be determined in the future.

After dechlorination of the SCCPs, the main reaction products in the oil phase from the separation tank were likely to be short-chain paraffins. In addition, trace amounts of aliphatic polymer were produced as a byproduct. These organic compounds need to be quantified by an instrumental analysis. It will also be important to assess the material balance of SCCPs in various parts of the system, including the exhaust gas from the reaction tank and water samples collected from the separation tank. Therefore, we will perform experiments based on a scaled-up SP method using a 20-L reaction tank.

Because we used GC-μECD to determine the LOQ of ΣSCCPs in this study, the maximum calculable DE was about 99.99%. However, 99.999% is the DE required for the chemical compounds listed in Annex A of the Stockholm Convention on POPs, including SCCPs, according to the general technical guidelines[1,10]. The long-term aim should be to decrease the LOQ of ΣSCCPs by one or two orders of magnitude (i.e., 0.023–0.23 mg/kg) through modification of the analytical procedure.

Acknowledgements

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