Songklanakarin J. Sci. Technol.
31 (6), 641-645, Nov. - Dec. 2009

Songklanakarin Journal
of Science and Technology

http://www.sjst.psu.ac.th

Original Article

Efficient sonochemical degradation of hexachlorobenzene in a model sediment

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Received 28 September 2007; Accepted 3 March 2009

Abstract

There has been increasing concern over contamination of the environment by persistent organic pollutants (POPs) such as polychlorinated biphenyls, dioxins and hexachlorobenzene (HCB), because of their highly persistent, bioconcentrative and toxic properties. In particular, the contamination of sediments may have a significant effect on the environment, because this contamination is closely related to the contamination of POPs in aquatic organisms.

In this study, the potential of sonochemistry for degrading HCB in a model sediment sample is evaluated. Further, the effects of ultrasonic irradiation and its combination with the Fenton reaction or the addition of a surfactant are examined.

Keywords: sediment, sonochemistry, ultrasound, nonionic surfactant

1. Introduction

Several spots such as harbours, canals and estuaries, particularly those near previous or current industrial sites, have been found to be contaminated by organic and inorganic contaminants.

In the long-term or on a global scale, sediments function as storage sites for nutrient salts in ponds, lakes and seas. However, in the short term or on the local scale, sediments act as resources by being dissolved in water or being bioconcentrated in aquatic organisms. Further, these sediments can easily be contaminated by organic contaminants. Hence, despite the imposition of new regulations on wastewater, which aid the protection of the environment by enforcing a reduction in contaminant emissions flowing into water, it is sometimes necessary to remediate the contaminated sediments (Meegoda and Veerawat, 2002; Hosomi, 2005).

In particular, there has been increasing concern over contamination of the environment by persistent organic pollutants (POPs), because of their highly persistent, bioconcentrative and toxic properties. Polychlorinated biphenyls (PCBs), dioxins, hexachlorobenzene (HCB) and some agricultural chemicals are classified as POPs. In 2004, the Stockholm Convention on POPs, which is one of the international conventions, entered into force.

HCB has been used as an agricultural chemical; further, it is released into the environment from by-products of the chemical industry. For example, an HCB contamination of approximately 50 ppm in soil was found in the vicinity of Wuhan city in China (Yuan *et al.*, 2006).

For all these reasons, it is necessary to develop effective methods for degrading and/or detoxifying POPs in

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sediments. Sonochemistry is potentially the core concept of a method for the remediation of sediments. Bubble growth results in the generation of hotspots; a hotspot is essentially a reaction field with temperature and pressure greater than 5,000 K and 1,000 atm, respectively (Suslick, 1990); therefore, pyrolysis and the production of radicals are accelerated. This is the chemical effect of sonochemistry, and its efficiency peaks when the frequency of irradiated sound is in the range of 200-500 kHz. The collapse of cavity causes generation of micro-jets that accelerate mass transfer. This is the physical effect of irradiated ultrasound, and it is considered that lower frequencies will be more effective in terms of the physical effect (Koda, 2004).

The objective of this study is to evaluate the potential of sonochemistry and its combination with the Fenton reaction or the addition of a nonionic surfactant, for degrading HCB in a model sediment sample.

2. Experiment

2.1 Chemicals and materials for experiments

The HCB reagent used in experiments was provided by Tokyo Chemical Industry Co., Japan. Cellulose powder was provided by Sigma-Aldrich, USA. Silica powder, Triton X-100 (TX-100), hexane (for dioxin analyses), hydrogen peroxide and silica gel particles were purchased from Wako Pure Chemical Industries, Japan.

HCB was selected as a model POP because it has a simple structure. HCB has a structure in which all H atoms of benzene are replaced by Cl atoms. Its main emission source is agricultural chemicals and by-products of the chemical industry. Therefore, high amounts of HCB are present in the environment (Yuan et al., 2006).

TX-100, or octylphenol polyethoxylate (structure: C_8H_{14}-C_6H_4-$O(CH_2CH_2O)_nH$), is a nonionic surfactant. This surfactant was selected for our study because it has been widely used in industrial applications and its use in remediation processes has been investigated (Meta-Sandoval *et al.*, 2002; Yang *et al.*, 2006)

2.2 Preparation of model sediment

A model sediment (average particle size: 28 μm) was obtained by mixing 80 mass% of silica and 20 mass% of cellulose powders. Then, 100 mL of hexane was mixed with several microlitres of a 1,000 mg/L of HCB/hexane solution, and the resulting mixture was added to a model sediment. After maintaining this mixture for 24 h at room temperature in order to facilitate the complete evaporation of hexane, a model sediment with an HCB concentration of 25 ppm to the solid was prepared.

2.3 Extraction test using ASE-100

To obtain the removal ratio of HCB in the model sediment, it is essential for the recovery ratio of HCB from the model sediment to be high and stable. In this study, HCB was extracted from the sediment sample using an accelerated solvent extraction system (ASE-100, Dionex Corporation, Japan), because conventional extraction methods such as the Soxhlet method require a long time for extraction.

To confirm the recovery ratio at various concentrations of HCB (9, 15, 20 and 25 ppm) in the model sediment, extraction tests were performed. In subsequent experiments, the model sediment, as well as the mixture with distilled water, were subjected to extraction. In the latter experiments, 50 g of the sediment and 500 mL of distilled water were filtrated. Before and after the extraction using ASE-100, the HCB concentration in the model sediment or the mixture was determined quantitatively by gas chromatography/mass spectrometry (GC/MS; Saturn 2200, Varian Technologies Japan Ltd.), since GC/MS has been widely used for analyzing the low concentration organic compounds in the environment.

2.4 Sonochemical degradation experiments with or without combination of ultrasonic irradiation with the Fenton reaction

Sonochemical degradation experiments were performed in a batch-type reactor made of glass, at the bottom of which an ultrasonic transducer (power: 100 W) was placed (Hayashi *et al.*, 2006). The height and diameter of the reactor were 153 and 130 mm, respectively. The temperature inside the reactor could be maintained by circulation of cooling water. A mechanical stirrer was used to mix the sample.

In the experiments, effects of the following factors on the HCB removal ratio were investigated:

1) Effect of the amount of sediment: Mixtures of 10, 20 and 50 g of the model sediment with 500 mL of distilled water were irradiated by an ultrasound with a frequency of 200 kHz for 60 min.

2) Effect of the combination of ultrasonic irradiation with the Fenton reaction: The combination of ultrasonic irradiation with the Fenton reaction results in the generation of a large number of OH radicals. The Fenton reaction occurs as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad (1)$$

The mixture of 20 g of the model sediment and 500 mL of distilled water was irradiated by 200 kHz ultrasound for 60 min. Liang *et al.* (2007) showed the considerable improvement of 4-chlorophenol degradation in aqueous solution using iron powder as ferrous ion source. Therefore, before ultrasonic irradiation, hydrogen peroxide and iron powder were added until the concentrations of 100 mg/L and 1.0 g/L, respectively, according to our previous result (Liang *et al.*, 2007). Fe^{2+} was given by the dissolution of added iron powder. Liang *et al.* (2007) also showed that the dissolution of iron powder was too much in strong acid solution. This means that removal of surplus iron ion and neutralization of solution should be carried out after the degradation treatment. Therefore, the effects of initial pH, 3.0 and 5.6, on the HCB removal ratio were investigated.

2.5 Desorption experiments by addition of nonionic surfactant

For the efficient desorption of HCB from the model sediment, the nonionic surfactant Triton X-100 was added to the model sediment and the following investigations were carried out:

1) Effect of the amount of added TX-100: 10, 20, 200, 400, 1,000, 4,000 and 10,000 mg/L of TX-100 were added to the mixture of 20 g of the model sediment and 500 mL of distilled water. The experimental time was fixed to 30 min. Another mixture of 1,000 mg/L of TX-100 and 20 g of the sediment was irradiated by a 47 kHz ultrasound from an ultrasonic machine (power: 140 W).

2) Effect of the ultrasound frequency: The mixture of 20 g of the model sediment, 500 mL of distilled water and 1,000 mg/L of TX-100 was irradiated using ultrasounds with frequencies of 28, 50, 100, 200 and 600 kHz. The charged power of each ultrasound was measured (Koda *et al.*, 2003) and controlled to be almost 50 W.

3. Results and Discussion

3.1 Recovery ratio of HCB determined using ASE-100

The recovery ratios of HCB present in various concentrations in the samples are shown in Figure 1. In this figure, 'model sediment' and 'mixture' imply the results of extraction tests of a model sediment made and a mixture of model sediment with distilled water. From this figure, it is observed that the recovery ratio is sufficiently high for all cases and that the HCB concentration has almost no effect on the recovery ratio.

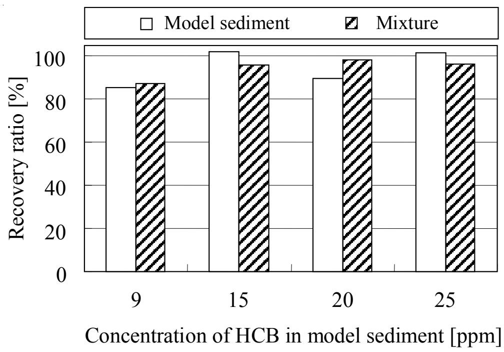

Figure 1. Effect of the concentration of HCB in model sediment on the recovery ratio of HCB.

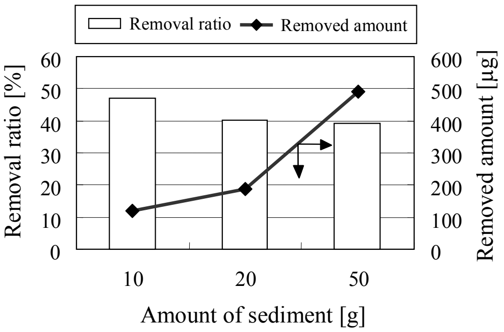

Figure 2. Effect of the amount of model sediment on the HCB removal ratio and removed amount.

3.2 Sonochemical degradation experiments

3.2.1 Effect of the amount of model sediment

The effect of the amount of model sediment on the HCB removal ratio is shown in Figure 2. Further, the actual amount of removed HCB is shown in this figure. Here, 'removal ratio' and 'removed amount' are used, since only the concentrations of remained HCB in the model sediment were measured. From this figure, we can observe that the amount of model sediment has almost no effect on the removal ratio but causes an increase in the amount of removed HCB. This behaviour might be attributed to the generation of ultrasonic cavitations throughout the reactor. For example, cavitations can occur at intervals of approximately 4 mm, which is the distance between the antinodes of the developed standing wave of 200 kHz ultrasound. In addition, the attenuation of ultrasound is little in the liquid; therefore, ultrasonic degradation can be carried out far from the ultrasonic transducer. This characteristic is desirable for the treatment of a large amount of sediment.

3.2.2 Effect of the combination of ultrasonic irradiation with the Fenton reaction

The effect of the combination of ultrasonic irradiation with the Fenton reaction on the HCB removal ratio is shown in Figure 3. From this result, we observe that the combination with the Fenton reaction has only a slight effect on the removal ratio. This behaviour might be attributed to the following:

In acid water, the ζ potential of silica particles becomes almost zero, as shown in Figure 4. When the absolute value of the ζ potential is less than 20 mV, the dispersed particles flocculate with each other because of a low electrostatic force and relatively high van der Waals' force (Leong, 2005). We can see that the ζ potential of silica particles is little less than -20 mV in the case of pH = 5.6. This means that the absolute value of ζ potential is little more than 20 mV. Therefore, flocculation phenomenon was not observed so much and the HCB removal was promoted. In this study, the flocculation of model sediment particles occurred and this phenomenon made sonochemical degradation more

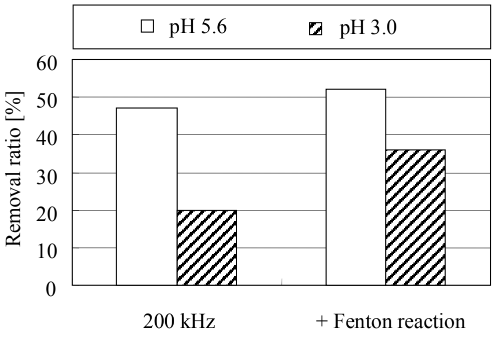

Figure 3. Effect of ultrasonic irradiation and combination with Fenton reaction on the HCB removal ratio.

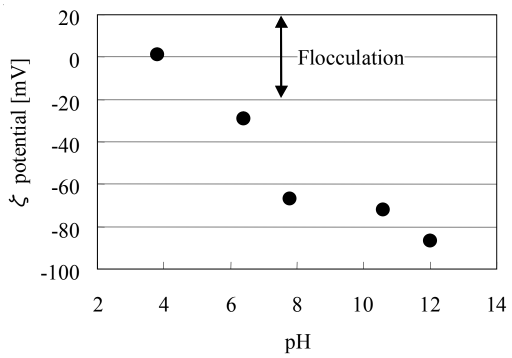

Figure 4. ζ potential of silica particles.

difficult.

Therefore, it appeared to be better to desorb HCB from the model sediment at the beginning. It can be easily imagined that the desorbed HCB in the liquid phase can be degraded efficiently by the combination of ultrasonic irradiation with the Fenton reaction (Liang et al., 2007). Therefore, desorption experiments were performed to investigate the following.

3.3 Desorption experiments using TX-100

3.3.1 Effect of the amount of added TX-100

The effect of the amount of added TX-100 on the desorption ratio of HCB is shown in Figure 5. The result of the combination of ultrasonic irradiation with the addition of TX-100 is shown in Figure 6, which also shows the effect of adding 0-1,000 mg/L TX-100. From Figure 5, it was observed that desorption ratio increased with an increase in the amount of added TX-100, and the optimum concentration of TX-100 for desorbing HCB was 1,000 mg/L. The critical micelle concentration (CMC) of TX-100 solution is approximately 125 mg/L (Wada, 2002), therefore, the value of 1,000 mg/L includes the absorption amount of TX-100 on the particle surface.

From Figure 6, it was observed that ultrasonic irradiation could result in an increase in the desorption ratio. This might be because of the physical effect of ultrasonic irradiation, *i.e.* enhancement of mass transfer of TX-100 and desorbed HCB molecules. Although it is thought that treatment for 30 min was enough for reaching the absorption - desorption equilibrium condition with ultrasonic irradiation, the desorption ratio was less than 50%. In order to promote the HCB desorption from the particles, the combination use of surfactants, *e.g.* TX-100 and dodecylbenzenesulfonic acid sodium salt (SDBS) (Yang *et al.*, 2006), and increase in the sample temperature are suggested as effective methods.

3.3.2 Effect of ultrasound frequency

The effect of the irradiated ultrasound frequency on the desorption ratio of HCB is shown in Figure 7. From the

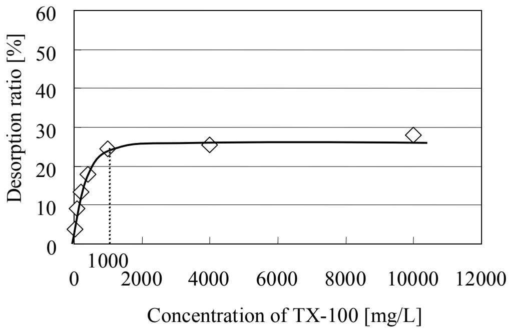

Figure 5. Effect of TX-100 addition on the HCB desorption ratio.

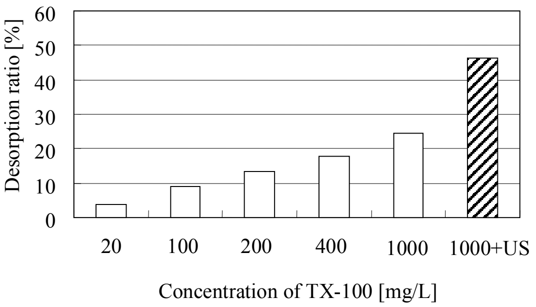

Figure 6. Effect of TX-100 addition and combination with ultrasonic irradiation on the HCB desorption ratio.

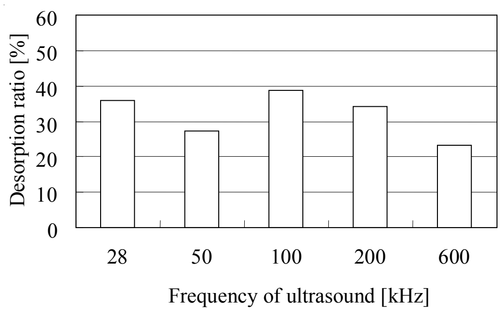

Figure 7. Effect of the irradiated ultrasonic frequency on the HCB desorption ratio.

figure, it was considered that the ultrasound frequency had only a slight effect on the HCB removal ratio.

4. Conclusions

In order to efficiently degrade HCB (a POP) in a model sediment, various experiments were performed (1) using ultrasonic irradiation, (2) by combining ultrasonic irradiation with the Fenton reaction, and (3) by combining ultrasonic irradiation with the addition of a nonionic surfactant. The following results were obtained:

1. The increase in the amount of the model sediment had only a slight effect on the removal ratio of HCB and caused an increase in the amount of removed HCB. This behaviour might be attributed to the generation of ultrasonic cavitations throughout the sample.
2. The combination of ultrasonic irradiation with the Fenton reaction had only a slight effect on the removal ratio of HCB, because of the flocculation of particles of the model sediment in acid solution.
3. The addition of a nonionic surfactant, TX-100, had a beneficial effect on the desorption ratio of HCB. In this case, the optimum concentration of TX-100 was 1,000 mg/L. The combination of ultrasonic irradiation with the addition of such a surfactant enhanced the desorption rate.

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