

Destruction of Polychlorinated Biphenyls under Subcritical Water Conditions in the Presence of Hydrogen Peroxide or Sodium Hydroxide

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Abstract—Polychlorinated biphenyls (PCBs) are toxic pollutants that need to be cleaned and removed from our environment. In this work we have investigated the destruction of PCBs using microwave heating, conventional heating PCBs in water-hydrogen peroxide or water-sodium hydroxide systems. After heating, liquid-liquid extraction of the reaction mixtures was conducted prior to GC analysis. Our results revealed that the degradation efficiency obtained by microwave heating ranged from 18% to 53%. Fortunately, PCB-118, PCB-156, and PCB-180 congeners were effectively degraded in subcritical water with hydrogen peroxide or sodium hydroxide. Higher concentration of hydrogen peroxide and longer heating time increased PCB degradation. Over 91% PCB degradation was achieved for all three PCB congeners after 6 hours of heating at 350 °C with 30% hydrogen peroxide in water. The concentration of sodium hydroxide in water had only a mild influence on PCB degradation. However, high temperature significantly enhanced the efficiency of PCB degradation in water-sodium hydroxide system. All three PCB congeners investigated were completely destroyed after heating in 0.2% sodium hydroxide at 350 °C for an hour.

Index Terms—Polychlorinated biphenyls, PCBs, destruction, subcritical water, hydrogen peroxide, sodium hydroxide.

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are man-made organic chemicals that consists of carbon, hydrogen and chlorine. Due to their high boiling point, stability, non-flammability and electric insulating properties, PCBs were used in hundreds of commercial and industrial applications. Polychlorinated biphenyls (PCBs) were extensively used in electrical, heat transfer, hydraulic equipment, plastics, pigments and other industrial applications from 1929 to 1979. They can also be easily found as insulators in electrical transformers and ships. As these equipment and appliances go through the aging process, they get rusted and PCBs are easily leaked into our environment and contaminated nearby waters, soils, and sediments [1]-[13]. PCBs have shown some serious adverse effect on immune system, reproductive system, nervous system, and endocrine system. Due to its carcinogenic effect on humans, US congress banned the production of PCBs in the late 1970's.

In order to decontaminate PCBs, several technologies include catalytic dechlorination of polychlorinated biphenyls in subcritical water using metal nanoparticles

[14]-[17], microwave-hydrothermal reaction [18]-[20], sodium dispersion methods [2], [21], reductive dechlorination in subcritical water [9], [22], and PCB destruction using zero-valent irons [9]-[14], [23], [24] have been developed. Subcritical water dechlorination in the presence of hydrogen donors has been used to treat paint spray [2], [5], [9]-[15]. Sub- and supercritical water oxidation has also shown to be an efficient technique for degrading PCBs [3], [5]-[8], [25].

In this study we investigated the destruction of three PCB congeners, PCB-118, PCB-156, and PCB-180 in subcritical water with the presence of hydrogen peroxide or sodium hydroxide. We compared the degradation of PCBs in 0% hydrogen peroxide, 5% hydrogen peroxide and 30% hydrogen peroxide at 350 °C for 6 hours, 0.2% sodium hydroxide, 1% sodium hydroxide and 5 % sodium hydroxide at 300 °C and 350 °C for 1 hour. We also investigated microwave effect on PCB destruction. Kinetic effect on PCB degradation was also investigated by using 1 hour and 6 hours of heating time. Stainless steel reactors were employed to hold the reaction mixtures during heating. Microwave degradation experiment was performed in glass tubes. After the thermal or microwave heating, the reaction mixtures are analyzed by gas chromatography.

II. MATERIALS AND METHODS

A. Reagents and Materials

PCB-118 (2, 3', 4, 4', 5-pentachlorobiphenyl), PCB-156 (2, 3, 3', 4, 4', 5-hexachlorobiphenyl), and PCB-180 (2, 2', 3, 4, 4', 5, 5'-heptachlorobiphenyl) were purchased from Accustandard (New Haven, CT, USA). Methylene chloride, p-xylene, and hexane were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Acetone was acquired from VWR International (West Chester, PA, USA). Hydrogen peroxide was purchased from Fisher scientific (Fair Lawn, NJ, USA). Sodium Hydroxide was purchased from Sigma-Aldrich (St. Louise, MO, USA). The microwave was purchased from Avanti Products (Miami, FL, USA). The 18 MΩ-cm deionized water was prepared in our laboratory using a PureLab ultra MK2 system from ELGA (Lane End, Buckinghamshire, England). Stainless steel vessels (7.07 mL, 9 cm x 1 cm ID) were purchased from Raleigh Valve and Fitting Company (Raleigh, NC, USA).

B. Preparation of PCB Stock and Working Solutions

The PCB stock solution was prepared by dissolving 5 mg of each of the three PCB congeners in 2 mL of hexane.

Manuscript received June 9, 2018; revised August 17, 2018.

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Each GC calibration standard solution was prepared on the same day when the heating mixtures were prepared. To prepare the calibration standard solution, 50 μL of the PCB stock solution, 1.5 mL of hexane, and 10 μL of p-xylene were added into an auto sampler vial.

C. Heating of Reaction Mixtures with An Oven

Stainless steel reaction cells were used for heating the reaction mixtures. The reaction cells were rinsed with acetone and allowed to dry completely before each use. Two layers of Teflon tape were wrapped around both ends of the cell. One end of the cell was tightly sealed with an end cap. First, 50 μL of the PCB stock solution was introduced to the reaction cell, and the hexane solvent was allowed to evaporate, leaving just the PCBs in the reaction cell. At this point, 3 mL of either pure deionized water, 5% hydrogen peroxide, 30% hydrogen peroxide solution, 0.2% sodium hydroxide, 1% sodium hydroxide or 5 % sodium hydroxide was added to each reaction cell. The other end cap was then placed on the cell and tightened with a vise to ensure a safe seal.

The loaded reaction cells were placed onto a metal tray that was then put into an oven. The reaction cells were heated at 300 or 350 $^{\circ}\text{C}$, each for 1 or 6 hours. After heating, the cells were removed from the oven and allowed to cool to the room temperature. The cells were then set standing and one end cap was removed. The reaction mixture was then transferred into a glass vial. The reactor was washed with 1.5 mL of methylene chloride and the wash was added to the same vial containing the reaction mixture. Liquid-liquid extraction was performed and the methylene chloride layer was then removed into a 4-mL vial. The methylene chloride wash and the liquid-liquid extraction were repeated and the methylene chloride wash was combined. Finally, 10 μL of p-xylene was added to the 4-mL vial as an internal standard for GC analysis.

D. Heating of Reaction Mixtures with Microwave

Glass vials (7 mL, Supelco, Bellefonte, PA, USA) were used in microwave heating experiment. The glass vials were rinsed with acetone and allowed to dry completely before each use. Exactly 50 μL of the PCB stock solution was introduced to the glass vial, and the hexane solvent was allowed to evaporate, leaving just the PCBs in the glass vial. At this point, 3 mL of pure deionized water was added into glass vials. Glass vials were placed inside the microwave oven and 1.2 KW, 60 Hz microwave was turned on for 5 min. After heating, the glass vials were removed from the microwave oven and allowed to cool to the room temperature. The reaction mixture in each heated vial was then transferred into another 7-mL vial. The microwaved glass vial was washed with 1.5 mL of methylene chloride and the wash was added to the same vial containing the reaction mixture. Liquid-liquid extraction was performed and the methylene chloride layer was then removed into a 4-mL vial. Finally, 10 μL of p-xylene was added to the 4-mL vial as an internal standard for GC analysis.

E. Gas Chromatographic Analysis

GC analysis was performed on an Agilent 6890 GC/FID (Agilent Technologies, Santa Clara, CA, USA) with an auto sampler. The injection amount for the analysis was 1 μL .

Split mode was employed. The initial oven temperature was 60 $^{\circ}\text{C}$. It was first increased to 250 $^{\circ}\text{C}$ with a rate of 25 $^{\circ}\text{C}/\text{min}$ and the temperature was held at 250 $^{\circ}\text{C}$ for 5 min before reaching the final temperature of 300 $^{\circ}\text{C}$ with the same heating rate. The oven was held at 300 $^{\circ}\text{C}$ for 5 min. Both the inlet and the flame ionization detector temperature were set at 300 $^{\circ}\text{C}$.

III. RESULTS AND DISCUSSION

A. Microwave Effect on PCB Degradation

We first studied the degradation of PCBs in pure water through microwave heating at 1.2 KW and 60 Hz for 5 min. Fig. 1 shows the percent degradation of PCBs under these microwave heating conditions. The degradation is 53%, 45%, 18% for PCB-118, PCB-156, and PCB 180, respectively. Because the microwave destruction of PCBs is not effective, we carried out further studies using subcritical water with addition of hydrogen peroxide or sodium hydroxide as discussed below.

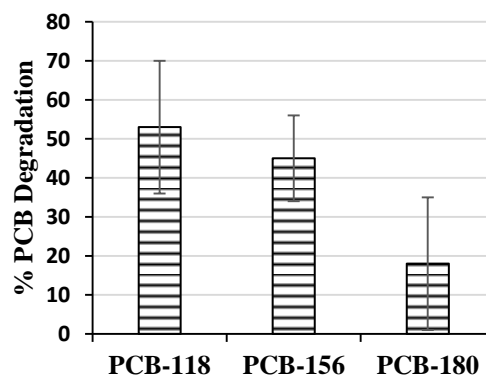


Fig. 1. PCB degradation in microwave after heating for 5 min.

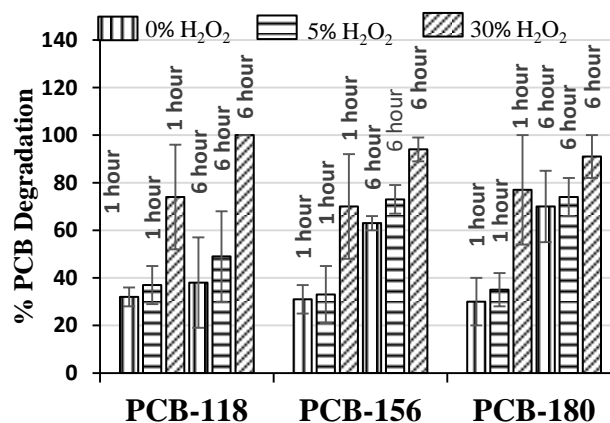


Fig. 2. PCB degradation in the presence of hydrogen peroxide after 1 hour and 6 hours of heating at 350 $^{\circ}\text{C}$.

B. Effects of Hydrogen Peroxide Concentration and Heating Time on PCB Destruction

Fig. 2 shows the effects of hydrogen peroxide concentration and heating time on percent PCB destruction at 350 $^{\circ}\text{C}$. It is clear that the percent degradation of all three PCBs studied increased with higher concentration of hydrogen peroxide. This trend was also confirmed by our

previous study [29]. Our kinetic study reveals that longer heating time yields higher efficiency for PCB destruction. As shown in Fig. 2, 100% PCB-118 was degraded at 350 °C with 30% H₂O₂ in water after heating for 6 hours, although the percent degradation of PCB-156 and PCB-180 is 94% and 91%, respectively.

C. Effect of Sodium Hydroxide Concentration on PCB Destruction

The concentration of sodium hydroxide has a mild influence on PCB degradation. As shown in Fig. 3, PCB degradation slightly increased when the sodium hydroxide concentration was increased from 0.2% to 1%. However, when the concentration of sodium hydroxide was further increased to 5%, there was no improvement in PCB degradation.

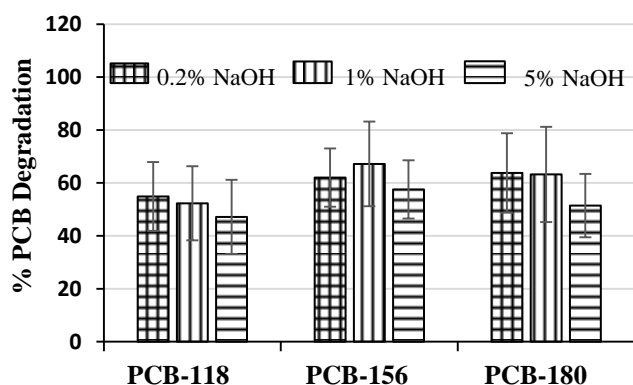


Fig. 3. PCB degradation in the presence of sodium hydroxide after 1 hour heating at 300 °C.

D. Temperature Effect on PCB Destruction in Water with Sodium Hydroxide

As discussed above, heating significantly enhanced the efficiency of PCB degradation in water-hydrogen peroxide system. Same trend was found in water-sodium hydroxide system. As shown in Fig. 4, all three PCBs investigated were completely destroyed after heating in 0.2% sodium hydroxide at 350 °C for an hour.

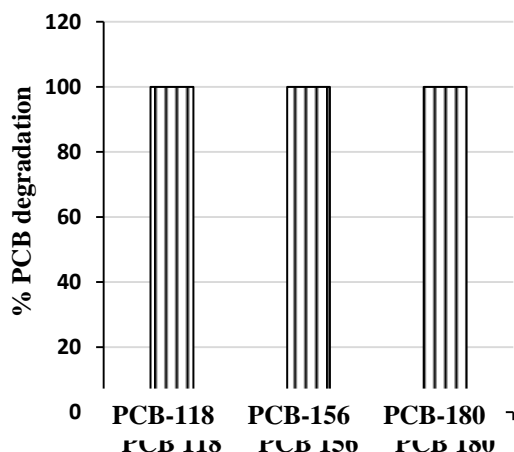


Fig. 4. PCB degradation in the presence of 0.2% sodium hydroxide after 1 hour heating at 350 °C.

IV. CONCLUSIONS

Our results indicate that the microwave heating in pure water is not effective in destroying PCBs. However, PCB-118, PCB-156, and PCB-180 congeners can be effectively degraded in subcritical water with hydrogen peroxide or sodium hydroxide. Higher concentration of hydrogen peroxide in water increases PCB degradation, and so is the prolonged heating time. The percent destruction of all three PCB congeners reaches over 91% after 6 hours of heating at 350 °C with 30% hydrogen peroxide in water. The concentration of sodium hydroxide in water has a slight influence on PCB degradation. Increasing temperature significantly enhances the efficiency of PCB degradation in water-sodium hydroxide system. It should be pointed out that all three PCBs investigated are completely destroyed after heating in 0.2% sodium hydroxide at 350 °C for an hour.

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