The Peroxy-Acid Treatment of Select Polychlorinated Biphenyls

by

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ABSTRACT

Polychlorinated biphenyls (PCBs) contamination has disrupted the quality of life for both aquatic and terrestrial beings. From water and soil contamination to occupational exposure, the toxicological effects of PCBs still cause harm today despite the ban on its production since the 1970s. This research investigates the applicability of the peroxy-acid method in the degradation of three selected PCBs (*e.g.*, 4-chlorobiphenyl, 2,2',4,4'-tetrachlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl).

The peroxy-acid method, an advanced oxidation process (AOP), was tested on PCB congeners 4-chlorobiphenyl, 2,2',4,4'-tetrachlorobiphenl, and 2,2',4,4',6,6'-hexachlorobiphenyl within an aqueous media. Initial testing, with an approximate 40 mg/L (concentration known) spike of 4-chlorobiphenyl in a solution of 1 mL of concentrated sulfuric acid (H_2SO_4) for catalysis of the peroxy-acid reaction, followed by a 5:5:5 mL (v/v/v) addition of 5 mL of a selected organic acid (formic, acetic, propionic, hexanoic, or malonic), 5 mL H_2O_2 (50% v/v), and 5 mL pure H_2O, determined that samples containing 500 mg of glass beads to serve as additional reaction surface area did not have an applicable effect on degradation of the PCB. 4-Chlorobiphenyl exhibited equal concentrations with and without the solid glass beads during the time course study. Thus, glass beads were not used for experiments in subsequent degradation analyses for 2,2',4,4'-tetrachlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl. Additionally, experimentation with formic acid was difficult to handle and was also eliminated in further studies. Gas chromatography equipped with a flame ionization detector (GC/FID) identified that propionic acid and malonic acid each demonstrated signs of success in the degradation 4-chlorobiphenyl through use of the peroxy-acid process. The pseudo first-order rate constants (k) were 0.0187 hr^{-1} and 0.0102 hr^{-1} for propionic and malonic acids, respectively.

Following the study of 4-chlorobiphenyl, the peroxy-acid method was performed for 2,2',4,4'-tetrachlorobiphenyl similar to that of the 4-chlorobiphenyl with the exception of eliminating the use of glass beads and formic acid. The method of analysis was also modified by switching from FID to electron capture detector (ECD) in an effort to better detect the multiple halogenated biphenyl. Estimated concentrations detected

by GC/ECD upon peroxy-acid treatment were insignificant compared to the initial spike concentration for all the organic acids tested. Thus, the best acid to degrade 2,2',4,4'-tetrachlorobiphenyl was inconclusive.

The degradation of 2,2',4,4',6,6'-hexachlorobiphenyl was studied with propionic and malonic acids as the organic acids to be tested in the peroxy-acid method. Such two acids were selected as they were observed to be most promising during the degradation study of 4-chlorobiphenyl. As with 2,2',4,4'-tetrachlorobiphenyl, the experiment was performed without glass beads and analyzed with GC/ECD. Both acids demonstrated degradation of 2,2'4,4',6,6'-hexachlorobiphenyl. The *k* values for propionic and malonic acids were determined to be 0.0060 hr^{-1} and 0.0041 hr^{-1}, respectively.

Propionic and malonic acids in the peroxy-acid method were observed to produce the most reliable and successful results in the degradation of 4-chlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl. Based on data obtained from the degradation of 4-chlorobiphenyl, positive correlations between *k* of the organic acids and molecular weight (MW), vapor pressure (VP), and aqueous solubility (S_w) of the organic acids were found. The correlation between *k* and VP was found to be most successful with a direct relationship and a correlation coefficient of 0.9968. Thus, the peroxy-acid treatment utilizing propionic and malonic acids as the organic acids was observed to be useful in the degradation of PCBs such as 4-chlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl but further studies are required to validate these findings.