

# Photochemical Dechlorination of Highly Chlorinated PCBs

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## Abstract:

This paper presents the results of a laboratory investigation to dechlorinate and degrade Aroclor 1254 using UV photolysis with and without a photosensitizer. Some experiments using Fenton's reagent as a pretreatment, prior to UV photodegradation, were also conducted. The impact of various solvents including hexane, alkaline isopropanol and neutral and alkaline acetonitrile on PCB photodechlorination, was studied. The results indicated that the rate of dechlorination was dependent on the solvent and the presence of alkalinity. Whereas dechlorination was observed in all solvents, it was most rapid in alkaline isopropanol. The dechlorination was marked by a chromatographic shift, observed in GC plots. The concentration of chloride ions released as a result of dechlorination was measured, in one instance, and found to increase with time. Irradiation with 254 nm UV light without any photosensitizer surfaced as the most effective method for dechlorinating Aroclor 1254. The biphenyl formed as a result of PCB dechlorination also degraded by photolysis. The treatment of PCBs with Fenton's reagent prior to subjecting them to UV irradiation, led to a decrease in Aroclor 1254 concentration.

## 1.0 Introduction:

Polychlorinated biphenyls (PCBs), which consist of 209 different congeners, are thermally stable organic compounds, which were widely used in capacitors, transformers, industrial fluids, fire retardants, inks, paints and pesticides (Hutzinger et al., 1974; Erickson, 1997). They were commercially manufactured and sold since 1929, as mixtures of congeners under different trade names, of which Aroclor® was the most common. The lipophilicity, environmental persistence and toxicity of PCB molecules have caused significant concern and led the USEPA to ban its usage in 1979. PCBs get adsorbed in soils and organic matter and enter the food chain through sediment dwelling microorganisms. Spills, legal and illegal disposal and uncontrolled use has caused an estimated one-third of the total US production of PCBs (about  $1.4 \times 10^9$  lbs) to be released into the environment (Wiegel and Wu, 2000). PCBs tend to bioaccumulate (bioconcentration factor of up to 73,000) and biomagnify as they move up the trophic ladder. The United Nations Environment Programme (UNEP) has identified PCBs as one of 12 persistent organic pollutants (POPs) that need international action. The acute and chronic health impacts of PCBs are extensive (Safe, 1994). The non-carcinogenic, chronic effects of PCBs could include damage to the liver, blood, immune system, nervous system and reproductive system.

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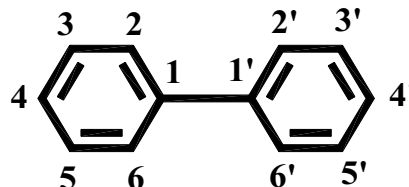
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PCBs are nonpolar, organic molecules having a biphenyl structure (i.e. two benzene rings bonded together by a single, nonpolar, covalent bond) with up to ten chlorine atoms bonded to the biphenyl framework. This arrangement of atoms yields the general molecular formula  $C_{12}H_{(10-n)}Cl_n$ , where  $n = 1$  to 10 (Erickson, 1997).



**Figure 1. Polychlorinated biphenyl molecular structure (Hutzinger et al., 1974)**

A number of remediation options for PCB contaminated soil and sediments have been investigated by different researchers. These include thermal processes such as desorption and incineration, chemical processes such as KPEG, KGME, base catalysed decomposition, and physical processes such as solidification, soil washing and solvent extraction. Recent research has focused on the photochemical dechlorination of highly chlorinated PCBs. The majority of photodegradation studies have used a catalyst to accelerate the rate at which chemical bonds are broken under exposure to natural or artificial UV light (Hawari et al., 1992; Zhang et al., 1993; Scudato and Chiarenzelli, 1995; Lin et al., 1995; Chiarenzelli et al., 1995). Using titanium dioxide ( $TiO_2$ ), as a photocatalyst, Zhang et al. (1993) achieved nearly an 80% reduction of PCBs in both aqueous solution and clay suspension after 4 hours of UV irradiation and 50% reduction in a sediment suspension within 6 hours. Chiarenzelli et al. (1995) were able to achieve up to 81% degradation of PCBs in contaminated sediment from the St. Lawrence River in a 24-hour irradiation period, while Scudato and Chiarenzelli (1995) reported that it was possible to degrade more than 85% of PCBs sorbed to soils and sediments within 4 hours. Nonetheless, the rate of degradation depends on the type of PCBs and the steric arrangement of chlorine atoms in the molecules. Sensitizers such as phenothiazine (PT) (Hawari et al., 1992) or diethylamine (Lin et al., 1995) have also been used to enhance the transfer of light energy to PCB molecules for photodechlorination. Successful hydroxylation of PCBs has been reported and a number of different hydroxylated chlorinated biphenyls have been identified. The oxidation of PCBs in aqueous solutions by hydroxyl radicals, generated during Fenton's reactions, has been reported by Sedlak and Andren (1991). The hydroxyl radicals get attached to one of the non halogenated sites, hydroxylating the PCBs. The addition of each hydroxyl radical improves PCB reactivity by promoting further attack of the molecules, by slightly electrophilic hydroxyl radicals (Sedlak and Andren, 1991). Dercova et al. (1999) found that the optimal oxidation of DELOR® 103 (equivalent to Aroclor® 1248) occurred in a solution containing 1M  $H_2O_2$  and 1 mM  $Fe^{2+}$ . Pignatello and Chapa (1994) were able to degrade 88 % of Aroclor 1242 using a photo assisted Fenton-type reaction. They found that the reactivity of the hydroxyl radicals decreases with an increase in PCB chlorination. Even though some successes have been reported, the remediation of PCB contaminated soils and sediments remain an area of active research.

This paper presents the results of a laboratory investigation on the photodegradation of highly chlorinated PCBs dissolved in different solvents and subjected to sensitized and non-sensitized

UV photoreactions. Results of studies that combined the action of Fenton's reagent with photodechlorination are also included.

## 2.0 Materials and Methods:

Three sets of experiments were conducted. These included:

- photolysis of commercial Aroclor 1254 in different solvent systems using UV with phenothiazine as photosensitizer
- photodechlorination of commercial Aroclor 1254 in alkaline isopropanol with and without hydrogen peroxide and the subsequent photodegradation of the biphenyls
- pretreating commercial Aroclor 1254 with Fenton's reagent for varying durations prior to photolysis with sensitized UV.

2.1 The solvent systems used for photolysis of commercial Aroclor 1254 using UV light sensitized with phenothiazine were:

- hexane
- alkaline (with 0.1N NaOH) isopropanol (IPA)
- acetonitrile - neutral and alkaline (with 0.1N NaOH)

Different concentrations of PCBs were prepared by dissolving neat Aroclor 1254 in known amounts of solvent. Subsequently, 5mM of phenothiazine (Hawari et al., 1992) was added to 10 mL of the solution in a 15mL pyrex tube. Initial zero hour samples, pertaining to zero hour reading, were taken out of the sample and stored for analysis. The headspace was then purged with nitrogen, and the sample was irradiated using 350nm UV light in a Rayonet UV photoreactor. Samples were collected at different time intervals and subsequently analyzed by a gas chromatograph (GC) equipped with an electron capture detector.

The samples in hexane and acetonitrile were injected directly into the GC for analysis. The samples in IPA were extracted using hexane and then analysed. The extraction was conducted by adding 10mL of water to each sample and pH of the sample was adjusted to between 5 and 6 by adding  $H_2SO_4$ . Once the pH had been adjusted, 10mL of hexane was added to the water-isopropanol mixture, and these samples were placed in a sonicator for 20 minutes. After 20 minutes of sonication, the samples were manually shaken for three minutes. Once the nonpolar and polar phases had separated, the hexane layer was transferred to a 40mL glass vial. Another 10mL of hexane were then added to the water-isopropanol mixture, and the extraction procedure was repeated (Hawari et al., 1992). The second separated hexane layer was combined with the first one, and the water-isopropanol layer was saved for chloride ion measurement, using a chloride selective electrode. The hexane was then evaporated to dryness in a fume hood using nitrogen. Then, 1mL of hexane was added to the vial to attain a final 1mL injection volume. These samples were analyzed using gas chromatograph with electron capture detection (GC/ECD).

2.2 The photolysis of commercial Aroclor 1254 using UV light at 254 nm wavelength in alkaline isopropanol was conducted under different alkalinity and with or without hydrogen peroxide. PCBs were dissolved in isopropanol and experiments were conducted under 3 conditions: 1) with 0.1N NaOH; 2) with 0.2N NaOH; and 3) with 0.1N NaOH along with 0.5mL

of 30% H<sub>2</sub>O<sub>2</sub>. Further, the experiment was repeated (only with 0.1N NaOH) at 3 initial Aroclor 1254 concentrations of 100ppm, 300ppm and 500ppm.

In these experiments UV light at 254nm was used. Since PCBs can directly absorb light with wavelength less than 300 nm, photosensitizers or catalysts were not used.

Varying amounts of neutral isopropanol were added to Aroclor 1254 to obtain known concentrations of solution. Nine milliliters of the solution were taken in a quartz tube and 110 $\mu$ L of 10N NaOH for 0.1N (or 220 $\mu$ L of 10N NaOH for 0.2N or 0.3mL of 30% H<sub>2</sub>O<sub>2</sub>) was added to the sample. The sample was well mixed by placing it in an ultrasonic bath for 1min. After sonication, duplicate 0.5mL samples were taken for zero hour readings. The sample was then irradiated with 254 nm UV light in a Rayonet UV reactor . Sampling was conducted at different time intervals, during UV photolysis, to examine Aroclor 1254 dechlorination patterns. Sample analysis was carried out using GC/ECD.

In a similar experiment, the amount of biphenyl produced as a result of PCB photodegradation, was monitored. The change in biphenyl concentration over time was studied using a GC/FID.

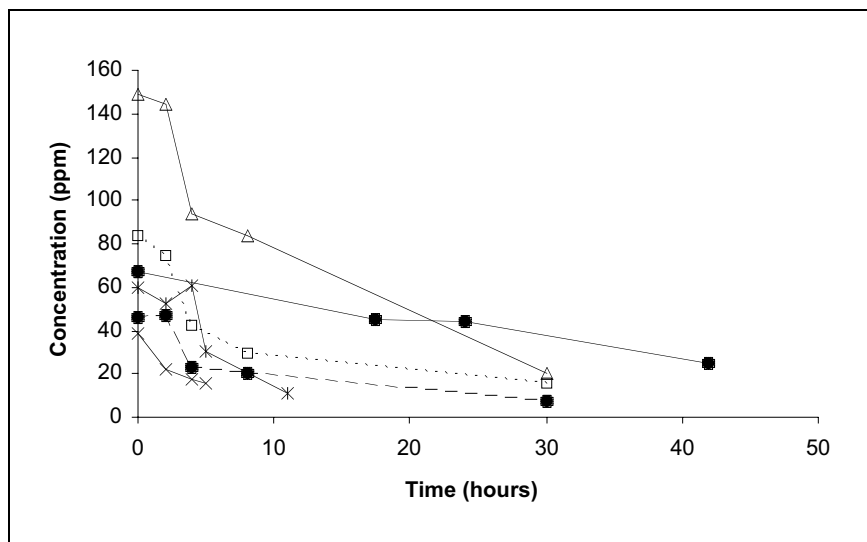
2.3 In another series of experiments commercial Aroclor 1254 was pretreated with Fenton's reagent followed by UV photolysis using phenothiazine as photosensitizer. A known amount of commercial Aroclor 1254 mixture was dissolved in hexane. The hexane was evaporated in a nitrogen environment and then 100mL of Fenton's reagent (Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub>; 1:1000; prepared by adding ferrous sulphate and hydrogen peroxide) was added to the flask. The sample was then placed on a rotary shaker at 26°C and 180rpm. Ten millilitre samples were withdrawn after a few minutes for a 0 day reading. The flasks were shaken for up to 12 days. Sampling was done at periodic intervals. PCBs were extracted from the samples using 10mL of a hexane:acetone (9:1; v/v) mixture. The extract samples were then placed in an ultrasonic bath for 20 minutes followed by shaking for 3 minutes in a separatory funnel. The organic layer was separated from the aqueous layer, and the process was repeated. The two organic layers were combined, centrifuged, and passed through Na<sub>2</sub>SO<sub>4</sub> to remove any remaining water from the sample (Dercova et al. 1999). The final sample volume was maintained at 10mL. Samples were analyzed for Aroclor 1254 concentration, using GC/ECD.

Five mM phenothiazine was added to 5mL of the sample pretreated with Fenton's reagent and irradiated using 350 nm UV light. After phototreatment, samples were again analyzed for Aroclor 1254 using GC/ECD.

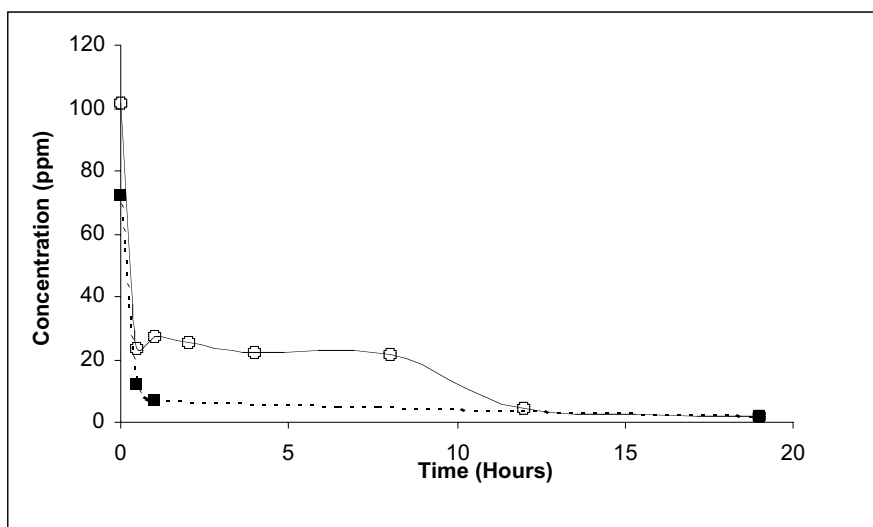
### **3.0 Results and Discussion:**

3.1 Photolysis of commercial Aroclor 1254 in different solvent systems using UV light sensitized with phenothiazine:

The experimental results are presented in Figures 2-4. The results indicated that for each solvent, Aroclor 1254 concentrations decreased over UV irradiation time, though at different rates. Of the three solvents, alkaline IPA seemed to have favoured the dechlorination the most. Unlike acetonitrile, PCB degradation in IPA was significantly enhanced in an alkaline phase.

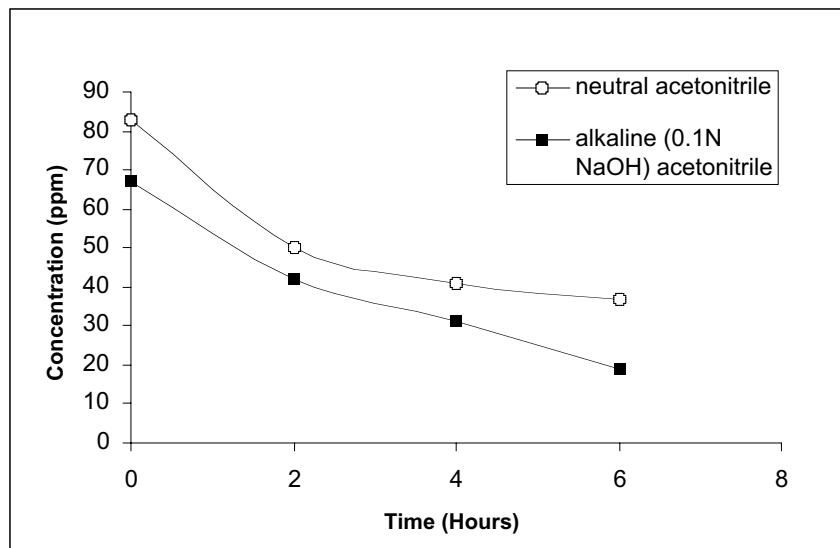


**Figure 2: Photodegradation of Aroclor 1254 in hexane using UV with phenothiazine as a photosensitizer (the plots refer to different initial concentrations)**



**Figure 3: Photodegradation of Aroclor 1254 in alkaline (0.1 N NaOH) IPA using UV with phenothiazine as a photosensitizer**

The irradiation results for commercial Aroclor 1254 in alkaline isopropanol indicated that the concentration decreased within 30 minutes to an hour of 350nm UV exposure, in the presence of phenothiazine. These results were similar to the findings of Hawari et al. (1992). The dechlorination of the highly chlorinated congeners was observed by a shift in peak retention time (data not shown). As the PCBs get dechlorinated, they are converted to lower chlorinated PCBs and then to biphenyl.



**Figure 4. Photodegradation of Aroclor 1254 in acetonitrile using UV with phenothiazine as a photosensitizer**

To ensure chloride ion release and biphenyl production, the chloride ion concentrations were monitored over time. Table 1 gives the increase in chloride ion concentration with time. A chloride ion peak was also detected when the sample was analysed using HPLC (data not shown).

**Table 1: Change in chloride ion concentration during Aroclor 1254 photodechlorination in alkaline IPA**

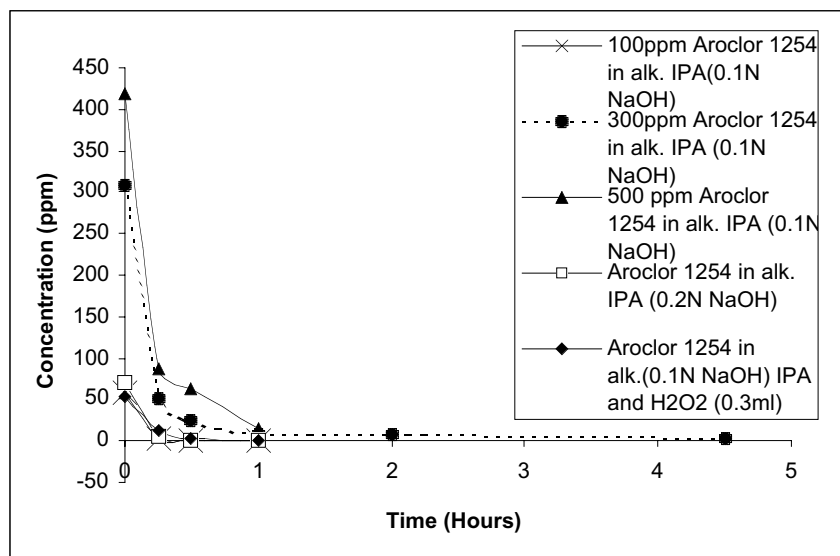
Time (h)	0	0.5	1	2	4	6	8	19
Chloride ion concentration (mg/L)	0.0	1.11	1.48	1.35	2.12	2.02	2.52	4.03

The samples were run on HPLC as well as a GC-MS to confirm the formation of biphenyl with subsequent PCB degradation.

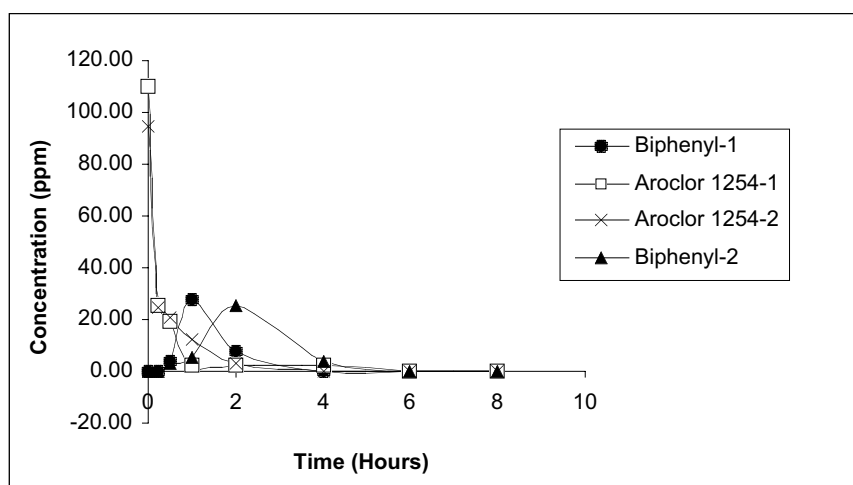
A high coefficient of correlation was observed when  $\ln[C]$  was plotted against time, indicative of the reaction being 1<sup>st</sup> order. The average reaction rate constants,  $k$ , were  $0.0898\text{h}^{-1}$  for PCBs in hexane, and  $0.1677\text{h}^{-1}$  for PCBs in acetonitrile. Similar results, supporting that the photolysis of PCBs follows first order reaction have also been shown by others. The photodegradation behaviour of PCBs in alkaline IPA was somewhat different from that in hexane and acetonitrile. It was marked by a sharp decrease followed by a gentle decline once the concentration had dropped off substantially.

3.2 Figures 5 and 6 show the progressive dechlorination of PCBs when UV light at 254 nm was used. This experiment was repeated with different initial concentrations, ranging up to 500ppm. Figure 5 depicts the photolysis results for Aroclor 1254 in the presence of higher NaOH concentrations and in the presence of  $\text{H}_2\text{O}_2$ . The plots illustrate the dechlorination of highly

chlorinated Aroclor 1254 congeners. Here again, the concentration fell sharply in the initial phase of the treatment. The reaction rate constants varied between  $0.9 \text{ h}^{-1}$  and  $7.3 \text{ h}^{-1}$ , which were significantly higher than those obtained from photodechlorination using UV at 350 nm with phenothiazine as a photosensitizer. The reaction rate constant was higher when  $\text{H}_2\text{O}_2$  was used ( $k=7.3 \text{ h}^{-1}$ ).

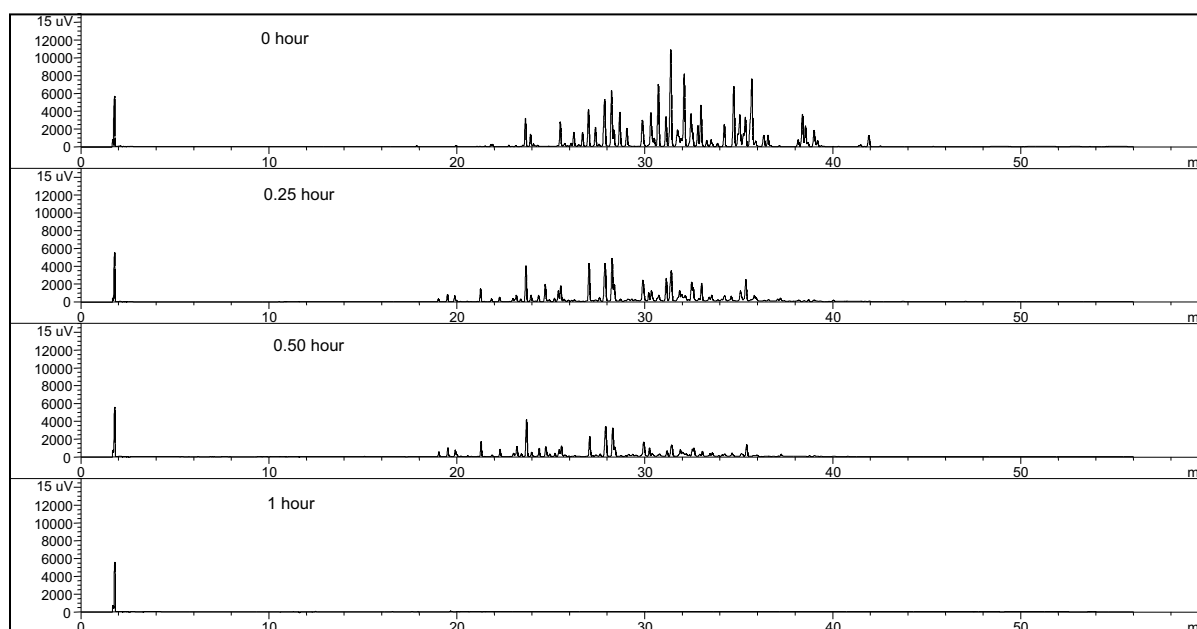


**Figure 5: Change in Aroclor 1254 concentration over time with exposure to 254nm UV light in an alkaline IPA environment**



**Figure 6: Change in Aroclor 1254 concentration and biphenyl (generated from Aroclor 1254 photolysis) concentration over time with exposure to 254nm UV light in an alkaline IPA environment**

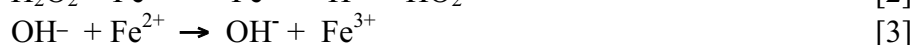
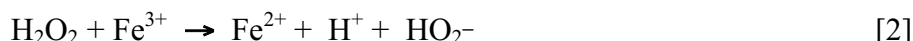
Figure 6, presents the results of duplicate experiments examining the photodegradation of Aroclor 1254 in alkaline IPA, where the change in biphenyl concentration was monitored parallel to PCB photodegradation. Chromatographs of the photolysis of Aroclor 1254, as shown in figure 6 (Aroclor 1254-1) are included in Figure 7. A review of the chromatographs indicates a sharp decrease in the concentration of PCBs even in the initial phase of treatment. Highly chlorinated Aroclor 1254 congeners, with peaks around a retention time of 30 minutes, get dechlorinated to lower chlorinated congeners eluting at lower retention times. This results in an increase in the concentration of the lower chlorinated congeners in the early stages of experiment. Subsequently, even the lower chlorinated congeners get dechlorinated and the peaks in the GC/ECD chromatographs diminish completely. Biphenyl molecules, produced once chlorine atoms have been completely stripped from PCBs, were observed, by GC-FID, within 30min of the photolytic treatment. As the PCBs dechlorinated, the biphenyl concentration increased. Eventually, the biphenyl also photolysed and its concentration started to decline. This phenomenon indicates that, not only was it possible to dechlorinate the PCBs, but the same system could potentially be used to also degrade the biphenyl molecules. The end products of the observed biphenyl degradation still require identification.



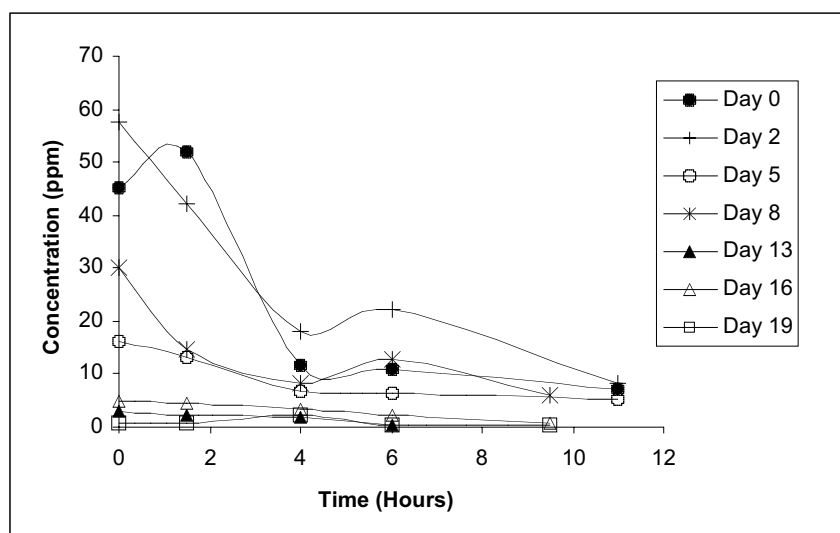
**Figure 7: Photolysis of commercial Aroclor 1254 over time with exposure to 254 nm UV light**

3.3 Fenton's reagent, a mixture of ferrous sulphate and hydrogen peroxide, generates  $\text{OH}^\cdot$  radicals, powerful non-specific oxidants formed as an intermediate products. Fenton's reactions, which involve the decomposition of hydrogen peroxide, by ferrous ions ( $\text{Fe}^{2+}$ ), to release hydroxyl radicals ( $\text{OH}^\cdot$ ), occur through a set of primary reactions. Some of these reactions are provided below (Walling, 1975):

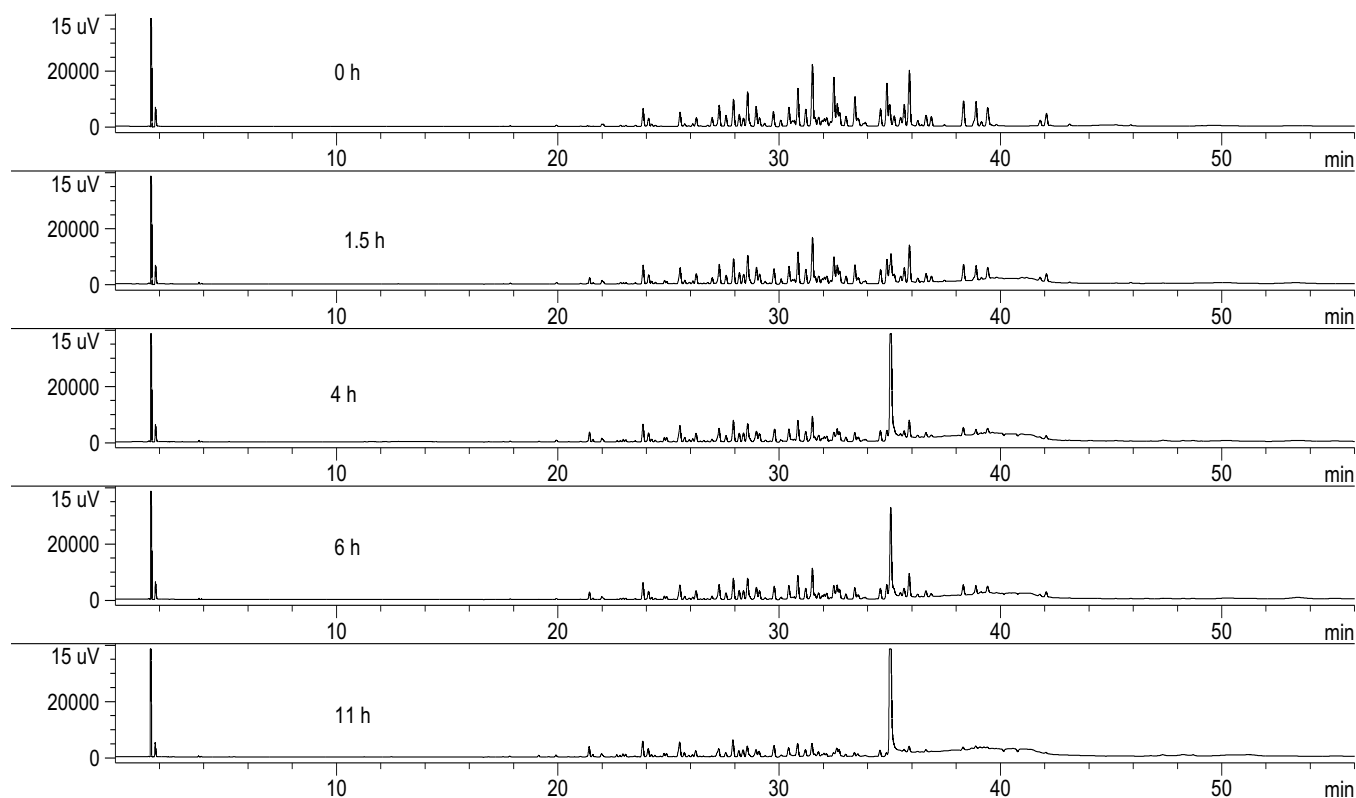




The reaction is exothermic and may be vigorous depending on the concentrations of hydrogen peroxide. The hydroxyl radicals are powerful oxidants. Sedlak and Andren (1991) have suggested that Fenton's reagent can oxidize PCBs in aqueous solutions. The hydroxyl radicals get attached to the non-halogenated sites on the benzene ring. The  $\text{OH}^-$  radicals can also attack the chlorine atoms in the ortho position. With time, and upon continuous contact, more hydroxyl radicals get attached leading to increased PCB ring cleavage. In our experiments, a decrease in concentration was observed when different amounts of PCBs were treated with Fenton's reagent for extended periods of time. Our experiments were conducted in two phases: a pretreatment of PCBs using Fenton's reagent, followed by photodegradation using sensitized 350nm UV light. The overall concentration of PCBs decreased with extended periods of contact with Fenton's reagent, as observed in Figure 8, and this may have been due to hydroxylation. The hydroxylated compounds of PCBs are non-volatile and go undetected via GC/ECD analysis. According to Sedlak and Andren (1991), dechlorination reactions are insignificant in comparison to hydroxylation reactions. This finding agrees with our observations, as total peak height decreased over time and no significant dechlorination shift was noted in the chromatograms. The plots shown in Figure 9 display the effect of UV photolysis in the presence of phenothiazine photosensitizer, following pretreatment with Fenton's reagent for different periods of time. Overlays of the chromatograms indicate a marginal shift towards a lower retention time,. An interesting phenomenon is the development of a sharp peak at a retention time of about 35 minutes. This finding requires further study.



**Figure 8: Photolysis of PCBs pretreated with Fenton's reagent for varying periods , using phenothiazine-sensitized, 350nm UV light (Note: in the legend, for example, Day 8 implies a Fenton's reagent pretreatment of 8 days)**



**Figure 9: Photolysis of commercial Aroclor 1254 with 350nm UV light and phenothiazine after 2 days of treatment with Fenton's reagent ( $\text{Fe}^{2+} : \text{H}_2\text{O}_2=1:1000$ )**

#### 4.0 Conclusions:

The following conclusions arose from this study:

- Photodechlorination of highly chlorinated PCBs is a viable technology, however the rate of dechlorination is dependent on the solvent characteristics;
- The rate of photodechlorination is highest in alkaline IPA, when non-sensitized UV light is used at 254 nm;
- Biphenyl molecules generated via PCB photodechlorination can also be degraded through UV exposure; and
- Fenton's reagent pretreatment decreases PCB concentration, and subsequent treatment with UV photolysis can lead to further concentration reductions; however, the lengthy time periods required by the Fenton's reagent process may make it impractical for field application.

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