

Photodechlorination of Aroclor 1254 in a Pilot-Scale Flow through Photoreactor

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Abstract: A novel pilot-scale flow through photoreactor has been designed with the intent to apply it in the field. The photoreactor uses a new plastic coil, instead of the conventional quartz tube. The photoreactor consists of six ultraviolet (UV) lamps with five around the coil and one at the center. Laboratory investigations were conducted using the photoreactor to treat neat Aroclor 1254 in alkaline isopropanol (IPA). The photoreaction is fast and efficient, even though the UV transmittances of the three plastic tubes investigated were lower than that of quartz. The reaction kinetics of the practical mixtures are explored. An analysis of five different constituent congeners of Aroclor 1254 indicated that higher congeners dechlorinate producing some of the lower ones, which are subsequently dechlorinated. The dechlorination of Aroclor 1254 was faster when water was added to the alkaline IPA–Aroclor solution.

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Introduction

The use of ultraviolet (UV) photochemistry to degrade organics has been, and continues to be, widely researched. As well, there are quite a few large- and small-scale commercial installations of UV treatment systems worldwide, mainly for disinfection. The UV systems that exist today are of two kinds: those in which the samples are held within the photoreactor, a batch process, and those in which the target sample flows through, having UV lamps installed parallel to the flow, a continuous flow process. The former ones are largely used for laboratory investigations whereas the latter ones are for laboratory and commercial applications. The two major issues in designing an effective photoreactor are: Maximizing the UV exposure to the target sample and ensuring uniformity of exposure. Due to high-energy demands these become quite important in case of recalcitrant organics and if the sample has some turbidity. In most applications, the target fluid is contained in quartz tubes, a brittle yet expensive material.

This paper describes a novel flow through photoreactor, which was designed to ensure uniform UV exposure to the target sample and at the same time maximize the exposure period. The photoreactor uses a nonbreakable plastic material and is designed for field applications. The paper further describes the results of an experimental program to photodechlorinate Aroclor 1254

(AccuStandard, New Haven, Conn.), a recalcitrant, commercial polychlorinated biphenyl (PCB) mixture, that had wide spread applications in transformer oils and capacitors, until its usage was banned about two decades ago. It is estimated that a third of the U.S. production of PCBs, about 1.4×10^9 lbs, has made its way into the environment (Weigel and Wu 2000). PCBs, which consist of 209 different congeners, are loosely classified as lower and higher chlorinated, depending on the degree of chlorination. The higher the degree of chlorination, the more recalcitrant the PCB molecule. Aroclor 1254, a highly chlorinated PCB mixture, is fairly recalcitrant and not amenable to easy degradation. Photodechlorination of PCBs, wherein the chlorine atoms are displaced efficiently when the PCB molecules are exposed to UV light, has indicated promise (Hawari et al. 1992). The dechlorination has been found to be fast and efficient in the right medium and has the potential for wide-scale field applications in treating PCBs extracted from soils and sediments. A free radical based chain reaction for the photolysis of Aroclor 1254 in alkaline isopropanol was also suggested (Hawari et al. 1992). The dechlorination process was thought to be initiated by the excitation of the aryl halide (ArCl) to the excited singlet state, $^1\text{ArCl}$, followed by intersystem crossing to the excited triplet state, $^3\text{ArCl}$, prior to dissociation to an aryl radical cation $\text{Ar}^{\bullet+}$ and a chloride ion, Cl^- . Sodium hydroxide was added to render the medium basic, a necessary condition for the reaction.

For the development of an effective field scale photodechlorination system, the reaction kinetics is necessary. The photodechlorination of Aroclors have sometimes been modeled as first-order decays at least on a short time scale (Shi et al. 1998). Whereas data from numerous photolysis experiments on pure compounds have generally indicated a first-order decay, it is still not clear whether such a model would hold for a mixture of congeners. Yao et al. (1997), investigating the photolysis of 3,3',4,4'-tetrachlorobiphenyl, found that as the highly chlorinated congener dechlorinated, lower chlorinated congeners (such as 3,4,4' triCB, 4,4' DiCB, and others) were formed which then subsequently dechlorinated. They traced a pathway for the dechlorination of 3,3',4,4'-tetrachlorobiphenyl to biphenyl in alkaline isopropanol. Chang et al. (2003) also reported that the

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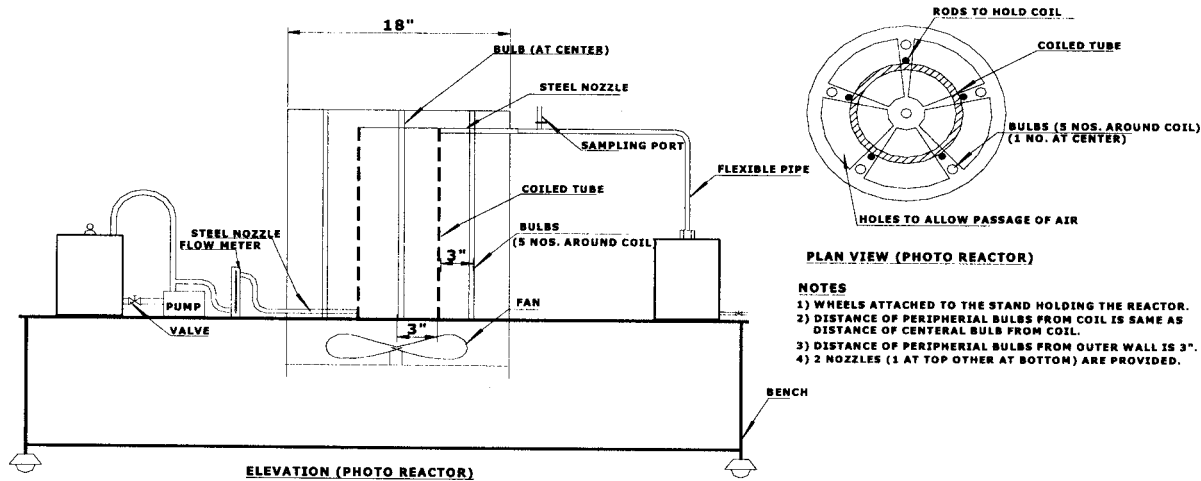


Fig. 1. Schematic of the flow through photoreactor

dechlorination of different higher chlorinated congeners in hexane led to the formation of lower chlorinated congeners, which eventually dechlorinate to biphenyl. Thus, in a mixture one would expect that as the concentrations of higher chlorinated congeners diminish, the concentration of the lower chlorinated ones would first increase, then decrease.

Here the design of a novel photoreactor, which involved novel polymeric material to carry the target fluid instead of the usual quartz, along with investigations on the dechlorination of neat Aroclor 1254 in the photoreactor, is presented. The fate of some of the different congener constituents of Aroclor 1254 when dissolved in alkaline 2-propanol, commonly known as isopropanol (IPA) and subjected to UV at 254 nm, has also been investigated and the applicability of first-order reaction kinetics to model reaction performances is discussed. Any system for photodechlorinating PCBs would require a prestep involving extraction of PCBs from contaminated soils and sediments. Since many PCB impacted sites have soil moisture or even free standing water which will get coextracted, it is necessary to investigate the impact of water on the photodegradation of the PCBs. Hence, Aroclor 1254 dissolved in alkaline IPA mixed with water and subjected to 254 nm UV light has also been investigated.

Photoreactor Design

Fig. 1 presents a schematic of a flow through photoreactor. The photoreactor consists of a coiled tube with five UV lamps on the outside and one UV lamp on the inside. The coiled plastic tubes used here were made of a material novel for this application, methyl vinyl ether modified tetrafluoroethylene (MFA) or ethylene-fluorinated ethylene propylene-co-polymer (EFEP) and were supplied by Markel Corporation, Plymouth Meeting, Pa. One tube made of MFA and two tubes made of EFEP were used. The MFA tube had a wall thickness and internal diameter of 1 mm and 1.9 cm, respectively. Two EFEP tubes with different wall thickness were used (0.64 and 0.12 mm). The MFA tube had a cloudy appearance as compared to the two EFEP tubes. However, none of the tubes were as visually clear as quartz suggesting scattering loss. The coil had an internal diameter of 15 cm (MFA and thin walled EFEP) and 16.5 cm (EFEP) and the length of the photoreactor is 70 cm. The internal diameter of both the EFEP tubes was 0.9 cm, almost half that of the MFA tube. The volume

of the target fluid in the illuminated zone was 2.2 L (MFA) and about 1.5 L (EFEP and thin walled EFEP). The length of the coiled tube inside the photoreactor was 760 cm (MFA) and about 2 m (EFEP and thin walled EFEP) giving the target fluid ample travel distance. The 254 nm UV lamps and the coil were encased in a stainless steel jacket making the diameter of the photoreactor 48 cm. At the base of the photoreactor, a fan was installed that could be switched on to prevent excess heating. The target sample reservoir was a plexiglass container outside the photoreactor fitted with a pump and a flow control valve. It was connected to the photoreactor with solvent resistant plastic tubing. The target fluid moves within the photoreactor from the bottom to the top, providing better control on the flow. Commonly, quartz is the preferred choice for the irradiation zone because of its high transmittance between 200 and 300 nm. However, quartz tubes, even though quite efficient in transmitting light (transmittance=0.93 or more), are brittle and expensive and difficult to form into a desired geometry. The present choice of plastic radically reduces the cost and risk of damage especially as this is intended to be applied in the field. The UV intensities within the chamber, measured by suspending a UV meter at different heights are given in Table 1. Even though the distribution of UV light within the chamber has higher intensities towards the center, the target sample within the closed coiled tube moving upward would

Table 1. Ultraviolet (UV) Intensities (mW/cm^2) at Different Locations within the Photoreactor

Location ^a	Inside the coil		Outside the coil	
	Facing inner bulb	Facing away from inner bulb	Facing outside bulbs	Facing away from outside bulbs
1	1.0	0.8	0.6	0.6
2	5.0	1.7	1.2	1.6
3	5.0	2	2	2.2
4	6.0	2.1	2.2	2.2
5	6.0	2.1	2.2	2.2
6	6.0	1.7	1.8	1.7
7	3.0	0.8	1.2	0.6

^aLocations 1–7 are equidistant points measured from the top of the photoreactor.

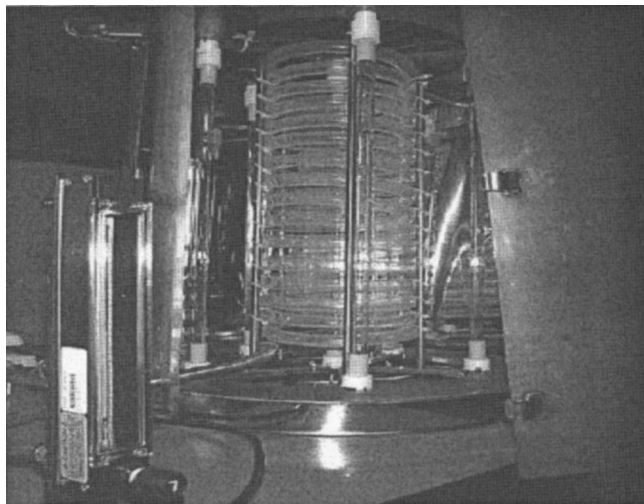


Fig. 2. Photograph of the flow through photoreactor

have a uniform exposure. Fig. 2 gives a picture of the flow through photoreactor. The UV intensities reaching the reaction zone of the different tubes investigated by actinometry were $1.95\text{E}+17$ photons/s (for MFA), $8.43\text{E}+18$ photons/s (for EFEP), and $1.06\text{E}+19$ photons/s (for EFEP, thin walled).

Experimental Protocol

Materials

Aroclor 1254 was purchased from AccuStandard, New Haven, Conn. For the purpose of calibration 1,000 L and 10,000 mg/L Aroclor 1254 stock solutions dissolved in isopropanol were prepared, whereas, for the experiments Aroclor 1254 obtained in neat form was dissolved in IPA in the laboratory and used at the concentrations obtained directly. Five specific congeners of Aroclor 1254, namely, 2,4,4'-trichlorobiphenyl, 2,2',3,5'-tetrachlorobiphenyl, 2,3',4,4'-tetrachlorobiphenyl, 2,3,3',4',6-pentachlorobiphenyls and 2,3',4,4',5-pentachlorobiphenyl were also purchased in neat form from AccuStandard. Other reagents were obtained from EMD Chemicals Inc., Gibbstown, N.J. All the solvents used during experiments were high pressure liquid chromatography grade and were used as purchased. Distilled deionized water was used wherever required in the experiments.

Instrumentation

All PCB measurements were performed using a Hewlett Packard (HP) 6890 series gas chromatograph with an electron capture detector. A DB-608 column with 30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness was used. Helium was used as a carrier gas with a flow rate of 1.5 mL/min and the samples were injected using a split ratio of 10:1. The samples were injected into the column at an initial temperature of 80°C which was then ramped to 180°C at $10^\circ\text{C}/\text{min}$. Beyond 180°C the temperature was further ramped at $3^\circ\text{C}/\text{min}$ to a final temperature of 270°C where it was held for 15 min. To ensure the integrity of the analytical measurements, quality control measures as per USEPA Method 8082 (1996) were followed.

Table 2. Flow Conditions

Tube characteristics	Experiment number	Flow rate (mL/min)
Methyl vinyl ether modified tetrafluoroethylene (MFA)	1	8
Ethylene-fluorinated ethylene propylene-co-polymer (EFEP)	1	5.8
	2	5.6
	3	6.0
EFEP (thin walled)	1	7.8
	2	7.9
EFEP (thin walled)	1 (70:30; IPA:water)	7.9
	2 (90:10; IPA:water)	7.8

Photolysis Procedures

Photodechlorination of Aroclor 1254 was attempted in the three different coiled tubes in the flow through photoreactor.

A 4L solution of Aroclor 1254 was prepared by dissolving 1 g neat Aroclor 1254 in isopropanol. The solution was made 0.1M alkaline by adding 40 mL of 10 M NaOH. The solution was then placed on a magnetic plate and stirred for half an hour to ensure homogeneity. The entire solution was used as an input to the flow through reactor.

Initial samples of 1 mL each were collected and analyzed for zero hour reading. The coiled tube in the photoreactor was then filled to the top with the aid of a pump. Flow rates during the experiments were maintained constant with a flowmeter and are presented in Table 2. Constant flow was also ensured manually by measuring the volumetric flow per minute. The UV bulbs of wavelength 254 nm were switched on as soon as the coiled tube was filled and the solvent started to flow through the other end of the coiled tube. Samples were collected at regular intervals from the sampling port located on the output side of the steel jacket during the experiment (Fig. 1). The Aroclor 1254 concentration was measured using the procedure recommended by USEPA Method 8082 (1996). The amounts of Aroclor 1254 dechlorinated were plotted as concentration with time of exposure.

The experiment with the MFA tube was conducted for 5 h with a flow rate of about 8 mL/min assuming that less transmittance will require longer UV exposure periods to completely degrade the PCBs. The experiments with both EFEP tubes were conducted for 3 h. Table 2 gives the flow rates for the different experiments.

In an extension to the isopropanol experiments, Aroclor 1254 was dissolved in IPA, which was then made alkaline with sodium hydroxide. Water was added to the IPA and the mixture of IPA and water was then homogenized by using a rotary mixer for 2 h. The mixture was then irradiated while flowing through the photoreactor. The purpose of this experiment was to determine the impact that moisture (e.g., from a soil sample) would have on the rate of photodechlorination. The experiment and the analysis were similar to that mentioned above.

Method of Analysis for Aroclor 1254

The analysis for Aroclor 1254 is performed following USEPA Method 8082 (1996). Aroclor 1254 concentrations were measured by considering the average area under 6 major peaks, at least one of which is specific to Aroclor 1254. In an Aroclor standard, those peaks are chosen that are at least 25% of the height of the largest Aroclor peak. A multipoint calibration graph is made by using those six peaks. The same six peaks are chosen in all the sample chromatograms for calculation of Aroclor 1254

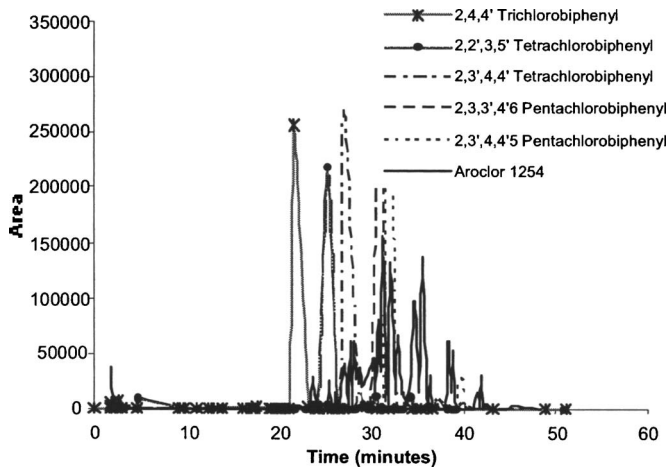


Fig. 3. Chromatogram of Aroclor 1254 along with identification of the peaks of the USEPA specified five congeners

concentrations. The gas chromatograms for Aroclor 1254 and several pure congeners are shown in Fig. 3. According to USEPA Method 8082 (1996), Aroclor 1254 is identified by the following five specific congeners: 2,4,4'-trichlorobiphenyl, 2,2',3,5'-tetrachlorobiphenyl, 2,3',4,4'-tetrachlorobiphenyl, 2,3,3',4',6-pentachlorobiphenyl, and 2,3',4,4',5-pentachlorobiphenyl. To analyze for Aroclor 1254, the area under at least one of these peaks should be considered. In these experiments, the concentration of each of these congeners was investigated. These individual congeners were also purchased from AccuStandard and their gas chromatograph signals are superposed on the ones obtained from neat Aroclor 1254 in Fig. 3. The chromatograms indicate that Aroclor 1254 contains a large number of congeners, many of which have higher chlorination than the ones considered above. It is clear that some congeners used to measure Aroclor 1254 could be formed during the dechlorination process.

For congener analysis, the concentration of each congener in the Aroclor 1254 mixture was determined by an area comparison given by

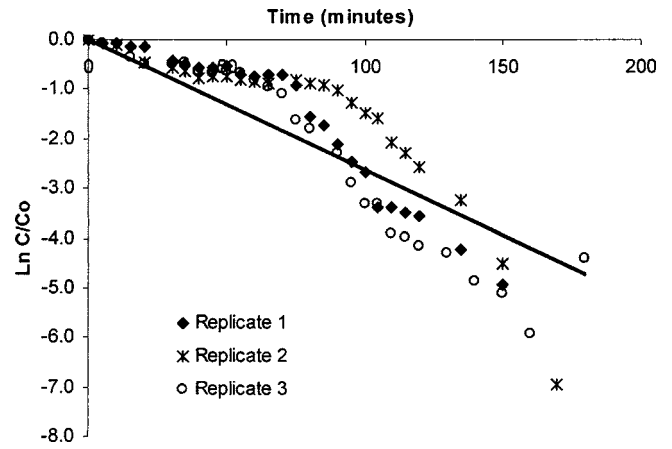


Fig. 5. Plot of natural logarithm of Aroclor 1254 concentration ($\ln C/C_0$) versus time in EFEP tube

$$\text{conc of congener} = \frac{\text{area of congener}}{\text{conc of Aroclor 1254}} \times \frac{\text{average area under 6 peaks representative of Aroclor 1254}}{\text{area of congener}} \quad (1)$$

The concentration of Aroclor 1254 was obtained from the average area of six major peaks using a calibration graph. The concentrations of the different congeners were calculated using Eq. (1) and hence do not represent actual values. They are therefore referred to here as pseudo concentrations and are used for comparative purposes only.

Results and Discussion

Kinetics

Aroclor 1254 loss was evaluated in the MFA, EFEP, and EFEP (thin walled) tubes. The sample flowed continuously through the coiled tube and the times recorded refer to residence time of the sample. All three tube choices give significant decrease in concentration with time, though the decrease is significantly higher

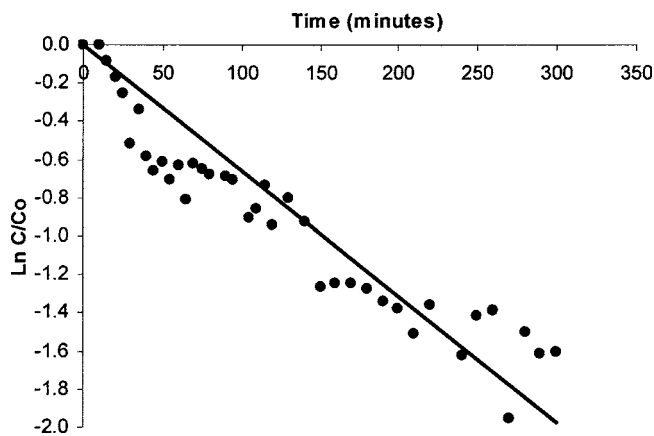


Fig. 4. Plot of natural logarithm of Aroclor 1254 concentration ($\ln C/C_0$) versus time in MFA tube

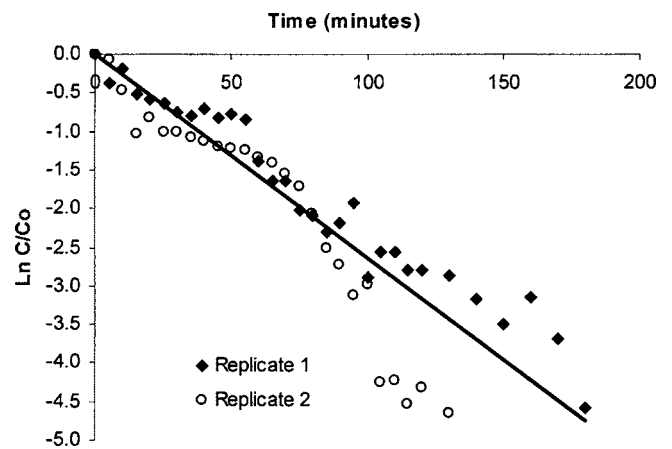


Fig. 6. Plot of natural logarithm of Aroclor 1254 concentration ($\ln C/C_0$) versus time in EFEP (thin walled) tube

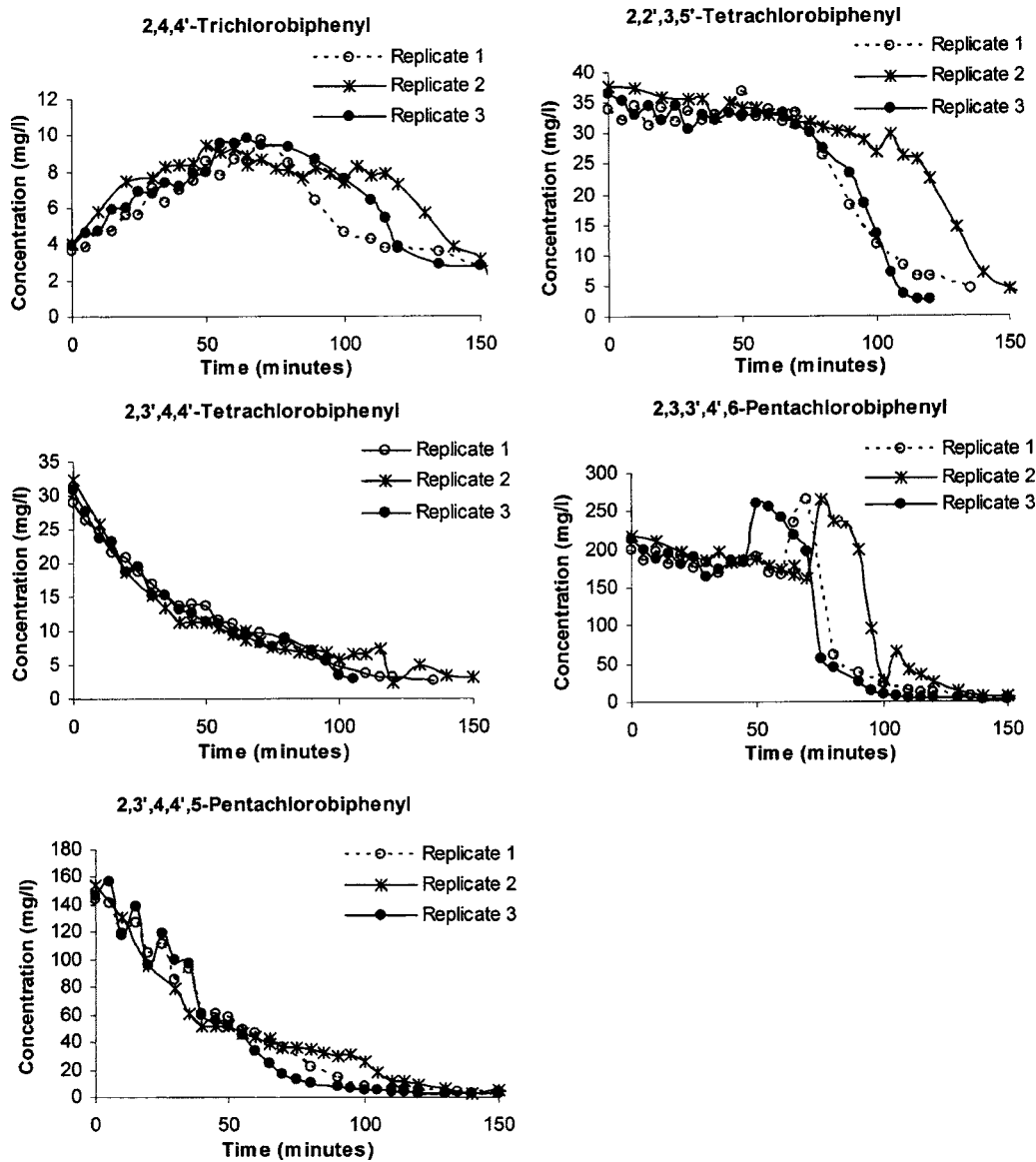


Fig. 7. Plots of pseudoconcentrations of different congeners of Aroclor 1254 when photodechlorinated in the EFEP tube

for both the EFEP tubes as compared to the MFA tube. Figs. 4–6 present the concentration time plots for Aroclor 1254 when dechlorinated in the MFA, EFEP, and EFEP (thin walled) tubes, respectively. The order was expected as the UV transmittance of the EFEP tubes is higher than that of the MFA tube. All the plots show a decrease that can be fitted approximately to pseudo-first-order kinetics. The rate constants so obtained were 0.4 h^{-1} for the MFA tube, 1.58 h^{-1} for the EFEP tube, and 1.6 h^{-1} for the EFEP (thin walled) tube. The coefficients of regression (r^2) for the plots were 0.82 for the MFA tube, 0.76 for the EFEP tube and 0.84, for the EFEP (thin walled) tube. These values imply practical “figures of merit” as follows: 99% reduction in Aroclor 1254 within 11.6 h of UV irradiation when contained in the MFA tube, 2.91 h when an EFEP tube is used, and 2.87 h when the EFEP (thin walled) tube is used. A 90% reduction in Aroclor 1254 concentration would occur within half this time, 5.8, 1.45, and 1.44 h for MFA, EFEP, and thin walled EFEP tubes, respectively. The poor statistics of the first-order plots are a consequence of the mixture character of Aroclor 1254. Single congeners are reported to exhibit first-order behavior (Chu and Kwan 2002, 2003; Mincher et

al. 2000). On the basis of the rate of reactions obtained, only 1.1 kW h of energy is needed to dechlorinate 99% of Aroclor 1254 in one gallon of alkaline IPA solution in the EFEP tubes. The MFA tubes have a higher energy demand of 3 kW h for the same dechlorination.

Figs. 7 and 8 present plots of the different congeners and the variation of their pseudoconcentrations with time for the EFEP and thin walled EFEP tube. It is interesting to note that the two pentachlorobiphenyls have different loss trends. The 2,3,3',4',6-pentachlorobiphenyl shows little loss during the initial periods. In contrast the loss of 2,3',4,4',5-pentachlorobiphenyl starts almost immediately. Similar results are obtained when the loss of 2,2',3,5'-tetrachlorobiphenyl is compared with that of 2,3',4,4'-tetrachlorobiphenyl. There are two reasons for this behavior and both are believed to be contributing. The dechlorination of 2,2',3,4,5'-pentachlorobiphenyl or 2,2',3,4,4',5'-hexachlorobiphenyl can lead to the formation of 2,2',3,5'-tetrachlorobiphenyl, making its production rate similar to its dechlorination rate. Lin et al. (1995) reported the production of 2,2',3,5'-tetrachlorobiphenyl during the photodegradation of

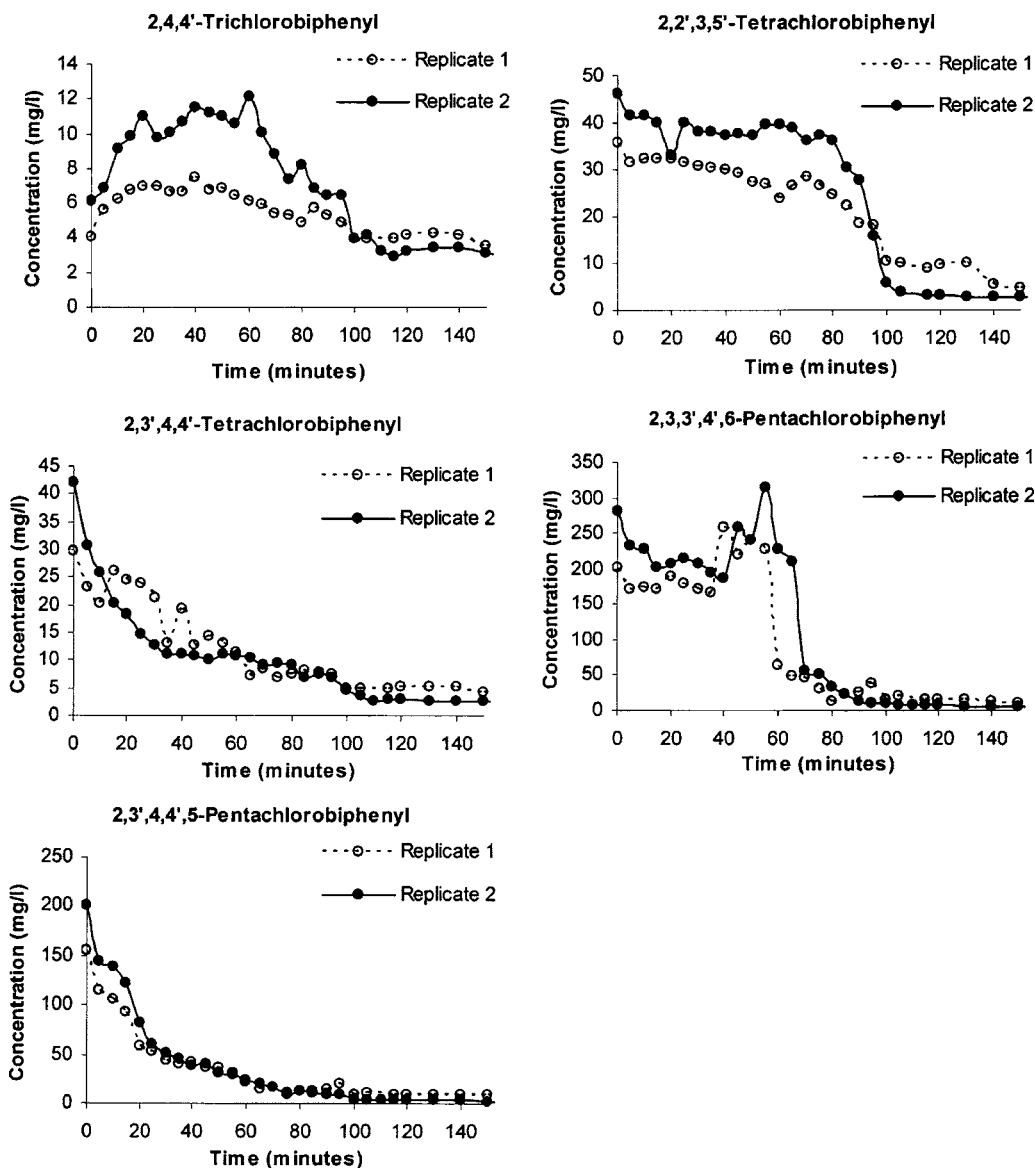


Fig. 8. Plots of pseudoconcentrations of different congeners of Aroclor 1254 when photodechlorinated in the thin walled EFEP tube

2,2',3,4,4',5'-hexachlorobiphenyl using simulated sunlight and diethylamine. 2,2',3,5'-Tetrachlorobiphenyl, one of the congeners investigated here, was shown as one of the dechlorination products of unsymmetrically substituted 2,2',3,4,5'-pentachlorobiphenyl (Miao et al. 1999). Similarly, the generation of 2,3,3',4',6-pentachlorobiphenyl upon dechlorination of 2,3,3',4',5,6-hexachlorobiphenyl not included in the five congeners investigated here explains the lack of initial concentration change. In fact 2,3,3',4',6-pentachlorobiphenyl tends to increase initially demonstrating its production. The amount of 2,3,3',4',5,6-hexachlorobiphenyl in Aroclor 1254 has been reported to be 1.03% (Frame et al. 1996). As the concentration of the precursors producing 2,3,3',4',6-pentachlorobiphenyl falls, its rate of formation drops and rate of loss dominates.

Lin et al. (1995), simultaneously studying the photodegradation of PCB congeners using simulated sunlight and diethylamine, reported 2,3',4,4',5-pentachlorobiphenyl as one of the dechlorination products (descendant) of 2,2',3,4,4',5'-hexachlorobiphenyl after 1 h of exposure to simulated sunlight. Frame et al. (1996) have reported that the concentration of 2,2',3,4,4',5'-

hexachlorobiphenyl in Aroclor 1254 is about 5.8% and those of 2,3',4,4',5-pentachlorobiphenyl and 2,2',3,5'-tetrachlorobiphenyl are 7.35 and 2.31%, respectively. Chang et al. (2003) reported the production of 2,3',4,4'-tetrachlorobiphenyl during the UV dechlorination of 2,3',4,4',5-pentachlorobiphenyl in hexane. The results presented here show a steady dechlorination of both the congeners indicating that rates of dechlorination are faster than the rate of generation through the dechlorination of 2,2',3,4,4',5'-hexachlorobiphenyl. Lepine and Masse (1990) had also reported the production of 2,3',4,4',5-pentachlorobiphenyls via orthodechlorination of 2,2',3,4,4',5'-hexachlorobiphenyl in petroleum ether and methanol. The 2,3',4,4'-tetrachlorobiphenyl upon irradiation can lose a chlorine atom at the 3' position to form 2,4,4'-trichlorobiphenyl. Chang et al. (2003) have reported the formation of 2,4,4'-trichlorobiphenyl during the UV dechlorination of 2,2',4,4'-tetrachlorobiphenyl and 2,3',4,4',5-pentachlorobiphenyl in hexane. There are other pathways as well that may lead to the formation of other congeners, not accounted for here, since Aroclor 1254 is a mixture of many congeners.

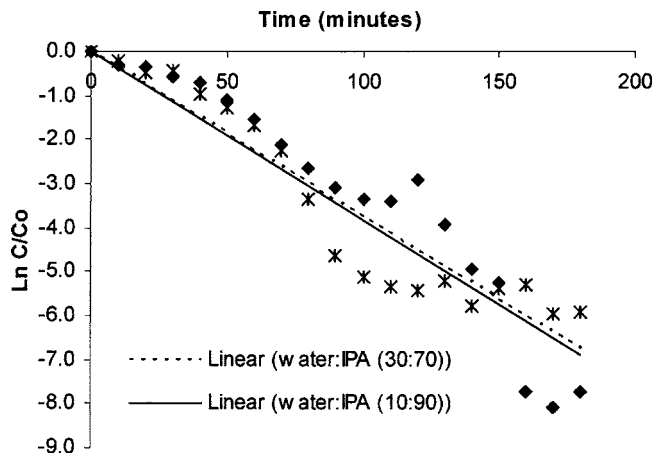


Fig. 9. Plot of natural logarithm of Aroclor 1254 concentration ($\ln C/C_0$) versus time in alkaline IPA–water mixture

The second factor can be differing recalcitrance of the different congeners toward dechlorination. It is known that the positions of chlorine atoms on the biphenyl ring determine the rate of chlorine loss from the congener. Hence two homologs with the same degree of chlorination but chlorine in different positions will have different rates of dechlorination. Yao et al. (1997) compared the photolysis rates of 3-chlorobiphenyl and 4-chlorobiphenyl reactions and found that the para chlorine is more readily released than meta chlorine. Steric congestion and asymmetry in arrangement of meta chlorine atoms also contribute to higher chlorine lability. Similar conclusions were arrived at by Chang et al. (2003), who reviewed research by Miao et al. (1999, 1996) on chlorine loss from PCBs in n-hexane and concluded that photoreactivities were lower in symmetrical and coplanar PCB congeners and that the reactivities were highest for ortho substituted chlorine, followed by meta and then by para substituted chlorine in PCB molecules. Research on PCBs

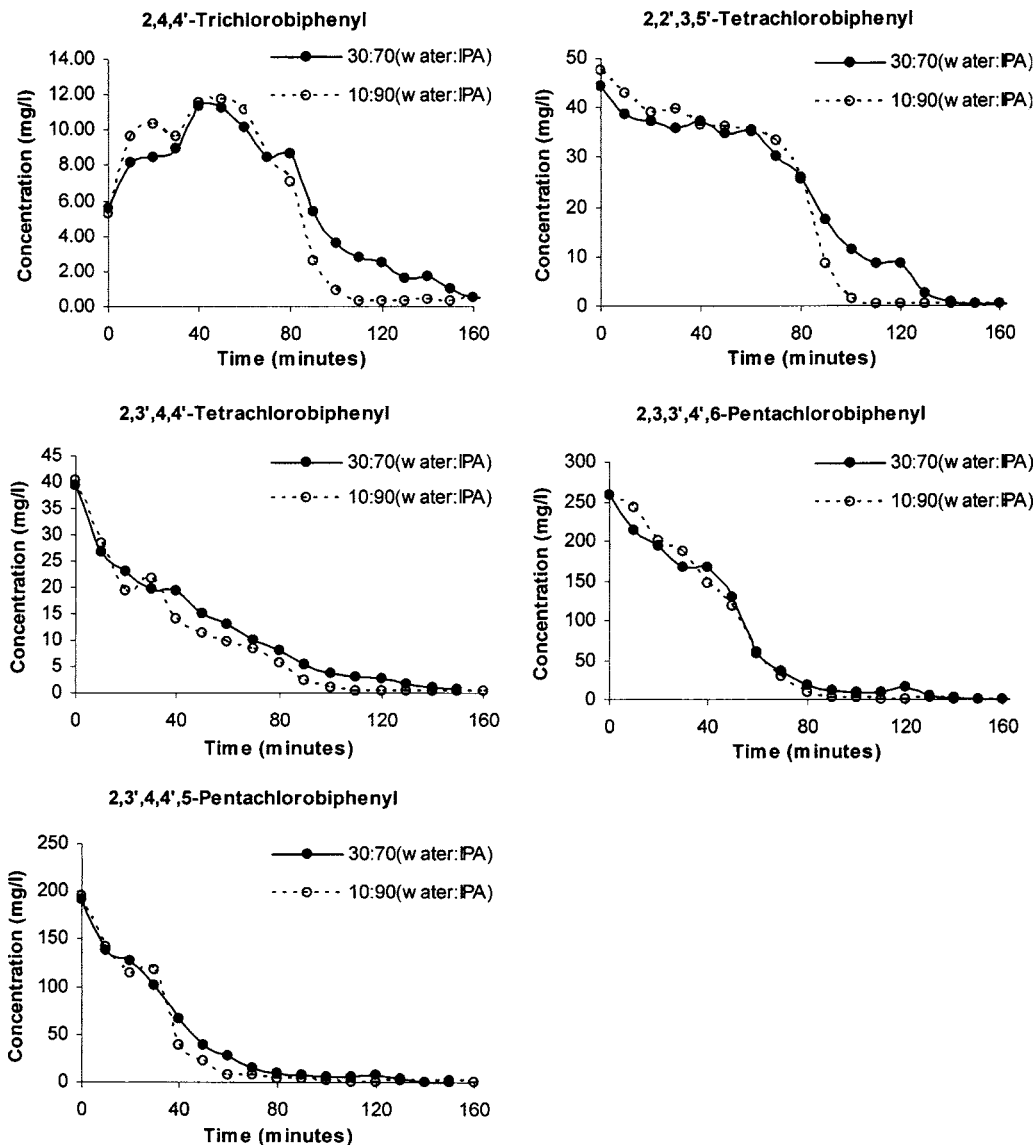


Fig. 10. Plots of pseudoconcentrations of different congeners of Aroclor 1254 in the presence of water when photodechlorinated in the EFEP tube

in n-hexane (Chang et al. 2003) has concluded that photodechlorination of PCBs occurred first on the benzene ring with greater chlorine number and on carbons which have higher negative atomic charge.

The concentration of 2,4,4'-trichlorobiphenyl, one of the lower chlorinated congeners in Aroclor 1254, shows an increase followed by a decrease. The increase in concentration implies generation of 2,4,4'-trichlorobiphenyl, upon the dechlorination of the penta- and tetrachlorobiphenyls. Formation of 2,4,4' via ortho dechlorination of 2,2',4,4' in methanol and in petroleum ether has been reported earlier (Lepine and Masse 1990). As higher congeners are depleted, the rate of dechlorination of 2,4,4'-trichlorobiphenyl becomes higher than the rate of generation, and its concentration starts to decrease. To model the concentration variations with time, rate of generation and dechlorination has to be considered, but for that the pathways of dechlorination need to be identified. Additionally, to conduct a quantitative analysis to determine rate constants, further investigations with pure congeners are necessary, since Aroclor 1254 provides many other congeners to consider. However, from an engineering perspective, data archiving via estimation of pseudo-first-order degradation kinetics may be sufficient, and can be used to approximate time for desired degree of dechlorination.

Water Effects

As wet soils are important, the effect of water on photodegradation in IPA must be examined. The change in concentration of Aroclor 1254 with time when water is mixed with the IPA is presented in Fig. 9. As mentioned previously, if the reaction kinetics is modeled as pseudo-first-order then the rate constants are: 2.2 and 2.3 h⁻¹ when 30 and 10% water were used, respectively. The coefficients of regression for both the plots are 0.89 and 0.9, respectively. Again, the use of first-order kinetics for mixtures seems a practical tool as it can provide an estimate of the percent dechlorination within a reasonable error. The reaction rate constants are somewhat higher than the ones obtained when water was not used, indicating that the presence of moisture helps in the photodechlorination of Aroclor 1254. This is believed to be due to water being a more favorable solvent system for proton transfer than IPA. Singh and Kremers (2002) have reported that the addition of up to 10% of water did not affect the dechlorination yield in radiolytic dechlorination of Aroclor 1254 and Aroclor 1016 in alkaline 2-propanol. However, the dechlorination yield did decrease when 25% water was added. Mucka et al. (1997) have also found no effect on dechlorination yields with 2% added water. Distilled water was used in our experiments. However, when PCBs are extracted from wet soils, the aqueous phase will contain impurities. These impurities may impact the photodechlorination.

Data with water for the five different congener variations with time are provided in Fig. 10. The trends of the congener dechlorination with time are similar. Here again, the 2,3,3',4',6-pentachlorobiphenyl shows a slower dechlorination initially compared to 2,3',4,4',5-pentachlorobiphenyl, which is lost faster. Similarly, the 2,2',3,5'-tetrachlorobiphenyl has an initial loss rate which is much lower than at a later time. This adds credence to our assumption that both 2,2',3,5'-tetrachlorobiphenyl and 2,3,3',4',6-pentachlorobiphenyl are being formed, as a product of dechlorination of higher congener PCBs, as they are dechlorinated.

Conclusions

The design of a new flow through photoreactor to treat significant volumes of organics has been presented. The photoreactor has potential for treatment of recalcitrant organics like PCBs in field conditions. The photoreactor uses novel plastic materials instead of quartz, which, although has a higher UV transmittance, is brittle and quite expensive making it costly for field applications. The photodechlorination of Aroclor 1254 dissolved in alkaline isopropanol was investigated in the photoreactor. Even though the UV transmittance of the three types of plastics were all lower than that of quartz they still demonstrated the potential of 99% dechlorination of Aroclor 1254 within a few hours. The changes in the concentrations of five congeners of Aroclor 1254 were also monitored. It was found that the dechlorination of higher chlorinated congeners led to an increase in the concentration of lower chlorinated congeners and that the rate of generation as compared to the rate of dechlorination determines whether the concentration would increase or decrease. These factors have an impact on the dechlorination kinetics of Aroclor mixtures and should therefore be considered. The use of pseudo-first-order kinetics to model the dechlorination of Aroclor 1254 gives approximate reaction rate constants as some of the constituents are dechlorinated as others are formed. The results of the experimental investigations indicate that PCBs, when extracted from soils and sediments, can be dechlorinated using this new photoreactor and the presence of some moisture will not hinder the performance.

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