Original Research Article

Removal of Polychlorinated Biphenyls (PCBS) From Soils Using Additives: Ambient Air Applications

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ABSTRACT

The aim of this study was to investigate the removal of polychlorinated biphenyl (PCB) compounds from the soil samples taken from around a cement plant in Bursa-Turkey. Ambient air applications were carried out, and the effects of titanium dioxide (TiO_2), diethylamine (DEA) and hydrogen peroxide (H_2O_2) on the removal of PCBs were determined. Firstly, the soil samples without any additives were exposed to ambient air conditions for 24 hours. Then, TiO_2, DEA and H_2O_2 were added to the soils at 1%, 10% and 20% of the soil dry weight. The PCB concentrations were measured using a gas chromatography-electron capture detector (GC-ECD). Only 2% Σ_{82} PCB removal efficiency was obtained in the sample prepared without using additive. This value reached 86% when 10% DEA was used as an additive. It was concluded that sunlight was not effective in the degradation of PCBs in soil without the use of additives and DEA was the most efficient photocatalyst for this study. Among the all ambient air applications, the 4- and 5- chlorine homolog group compounds were removed at the maximum ratio, while the 8- and 9- chlorine homolog group showed the lowest removal efficiency.

Keywords: TiO_2, DEA, H_2O_2, Soil, Sunlight, Photodegradation

INTRODUCTION

A variety of anthropogenic and natural pollutants has increasingly accumulated in soil and they alter the natural balance of the soil. In particular, rapid industrial growth and population increase in developing countries, such as Turkey, has led soil pollution to become a bigger environmental problem. Soil is an environmental marker that reflects the quantity and spatial distribution of semi-volatile organic compounds (SVOCs), such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) (Cetin 2016, Garcia et al. 2012, Ortiz et al. 2012) Soil is an important source of PCBs in the atmosphere and plays an important role in the global cycle of PCBs by acting as a reservoir (Ogulmus 2012). PCBs, which cause pollution in soil, have been examined by various researchers in different countries (Melnyk et al. 2015). They are classified as persistent organic pollutants (POPs) and known to be carcinogenic. Brawn (1987) showed that all Arochlor mixtures cause cancer in the liver of mice as well as promoting cancer diseases in the liver, gallbladder, and bile duct, by taking part in cancer production. In the Stockholm Convention, the use of PCBs was limited and even prohibited due to their negative impact on the environment and human health (Dönmez 2012). Therefore, they need to be removed from any kind of environment, such as air, water and soil.

SVOCs can be removed from soils in various ways (Jelic et al. 2015, Lin et al. 2013, Shaban et al. 2016). One method is through photodegradation with sunlight (Karaca and Tasdemir 2015). It is known that SVOCs in solid matrices, such as soil and treatment sludge, can be removed using different light sources, such as sunlight and UV light (Salihoglu et al. 2012, Zhang et al. 2008). To improve the photodegradation efficiency, additives like TiO_2, DEA and H_2O_2 can be used (Karaca 2013, Zhao et al. 2004). TiO_2 is a photocatalyst that accelerates the degradation of SVOCs by producing OH· radicals when stimulated by light source (Karaca and Tasdemir 2011). In addition, DEA is an effective photosensitizer that acts as an electron source (Lin et al. 2004). H_2O_2 is a chemical which contributes to the photodegradation process by producing OH· radicals when stimulated by sunlight. The present study aimed to specify the impact of various additives (TiO_2, DEA, and H_2O_2) on the removal of PCBs from soil samples taken near a cement factory in ambient air conditions. Within this scope, the most effective additive and its dose was determined. In addition, the removal efficiencies of PCB homolog groups were evaluated.

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MATERIALS AND METHODS

Soil sampling and characterization

Composite soil sample was obtained by mixing samples taken from 4 different points in the surface soil (0-5 cm) within an area of approximately 10 m^2. Stones and plants were removed from the sample, which was then wrapped in aluminum foil and stored in air-tight plastic bags. The soil temperature was measured during the sampling. Instantaneous and cumulative UV-A and UV-B values were determined using a Delta Ohm Multifunction Datalogger DO9847 (UV-A and UV-B probes), and the global radiation was measured (295-3000 nm) with a Delta Ohm LPPYRA02 pyranometer. 10 grams of the sieved (2 mm) soil was weighed and PCB pre-analysis steps were applied to the sample. Initial PCB concentrations of the soil sample were measured by GC-ECD. Detailed soil characterization data are presented in Table 1. Two grams of soil was added to 5 mL pure water (1/2.5), and the pH value was measured with a Metler Toledo Marka pH meter. Two gram samples were weighed and kept at 105 °C for 24 h. The final weight was measured and the dry matter (DM) was calculated. The total organic carbon (TOC) content of the sample was determined according to the standard method (Method 5310B) by using an SSM-5000 Shimadzu TOC analyzer (TOC-V CPN).

Table 1. Soil characterization.

Parameter	Value
pH	10
Soil Temperature	16 °C
Solid Matter	88 %
Total Organic Carbon (TOC)	2,7 %
Σ_{82} PCB	17 ng/g DM

PCB removal applications

PCB removal applications were carried out in the soil samples taken from the area around the cement factory. In this content, four sample groups were prepared. The first sample group did not include any additives. The other samples were prepared with additives to enhance PCB removal. TiO_2, DEA and H_2O_2 were dosed to the soil at 1%, 10% and 20% of the soil dry weight. The surface area of TiO_2 was ~50 m^2/g with an average particle diameter of 20 nm, a density of 0.1 g/cm^3 and a pH of 4. Density of DEA ($CH_3CH_2NHCH_2CH_3$) was 0.7 g/cm^3 (at 20 °C), and the pH was 13. Ambient air applications were carried out simultaneously in the soil samples with and without additives. Ten-gram soil was laid out the Petri dishes (with or without additive) and then placed outside (ambient air conditions) for 24 hours. At the end of each PCB removal application, the samples were subjected to pre-analysis and the residual PCB concentrations were measured by a GC-ECD. The removal efficiency was calculated by taking into account the residual PCB concentration in the soil and the initial PCB amount. The variables and additive doses are given in Table 2. All PCB removal applications were performed in 2 replicates, and the average values were used in the calculations.

Table 2. PCB Removal Applications.

Purpose	TiO_2 Dose (%)	DEA Dose (%)	H_2O_2 Dose (%)
Determination of ambient air effect	0	0	0
Determination of the effect of TiO_2	1	0	0
	10	0	0
	20	0	0
Determination of the effect of DEA	0	1	0
	0	10	0
	0	20	0
Determination of the effect of H_2O_2	0	0	1
	0	0	10
	0	0	20

PCB extraction, cleanup and determination

Five kilograms of soil was taken from the area around the cement factory, and this soil was used in all of the PCB removal experiments. The soil was transported to the laboratory in glass containers and homogenized by stirring with a glass rod for approximately five minutes. For testing, 10 g of the sample was taken from the original 5 kg for each run. The sieved (2mm) soil sample was weighed and placed in a glass bottle after adding 30 mL of dichloromethane/petroleum ether (DCM/PE) (1:1, v/v). Then, 1 mL of the surrogate standard was added to each sample. The samples were shaken at 280 rpm in an orbital shaker for 5 hours and afterwards were extracted for 30 minutes at a temperature of 15 °C in an Elma S 80H ultrasonic bath 2 times. The extracted samples were filtered through a Sartorius Stedim (FT-3-1103-047) glass microfiber filter. Following this, solvent exchange was performed in a rotary evaporator. The samples were concentrated to 5 mL in the rotary evaporator. Then, 15 mL of hexane (HEX) was added to the sample for solvent exchange, and the volume was again decreased to 5 mL. Then, the sample volume was reduced to 2 mL under a gentle nitrogen stream. The cleaning column used for fractionation was prepared as follows: the first layer consisted of glass wool, the second layer consisted of 3 g silicic acid then 2 g alumina, and the top layer consisted of 1 cm Na_2SO_4. Pre-elution was conducted using 20 mL DCM and 20 mL PE. After adding 2 mL of the sample, the first fraction (PCB) was collected using 25 mL PE, and the second fraction (PAH) was obtained with 20 mL DCM. The sample volume was reduced to 2 mL using a gentle nitrogen stream in two steps. The PCB samples were washed with H_2SO_4 to prevent the accumulation of any organic matter. Then, the sample volume was reduced to 1 mL by utilising a gentle nitrogen stream before being transferred into a vial. The program used during the analysis was as in Sakin and Tasdemir (2016) study.

Quality assurance/Quality control

Blank samples were taken up to 10% of the total number of samples to determine if there was any contamination during sampling and other operations. A 30 mL DCM/PE (v/v:1/1) mixture and 1 mL of the surrogate standard were added to all of the blanks and stored at -16 °C until analysis. The PCB surrogate procedures performed on the soil samples were also applied to the blanks. PCB#14, PCB#65, and PCB#166 congeners were added (1 mL) to the samples as surrogates. All glass materials were cleaned by DCM or HEX to prevent contamination. The limit of detection (LOD) was defined for each PCB compound. The LOD was calculated by adding 3 standard deviations to the average of the field blanks. Sample quantities exceeding the LOD were quantified and corrected by subtracting the mean blank amount from the sample amount.

RESULTS AND DISCUSSION

PCB removal by ambient air applications

Only 2% removal in the Σ_{82} PCB concentrations was obtained in the soil samples exposed to ambient air conditions without addition of TiO_2, DEA and H_2O_2. During the experiment cumulative UV-A, UV-B, and global radiation values were measured as 198, 13 and 15.030 kWs/m^2, respectively. It was seen that these radiation values were not sufficient to degrade PCBs in the soil. Similarly, researchers (Karaca and Tasdemir 2015, Karaca G. 2015) could not be removed PAHs from treatment sludge and soil without using additives under ambient air conditions (24 hours). The impacts of the photocatalyst (TiO_2, H_2O_2 and DEA) on the removal of PCBs were given in Figure 1. The highest Σ_{82} PCB removal ratio was calculated as 86%, which was obtained by the addition of 10% DEA. In the samples containing DEA and H_2O_2, 10% was the most effective dose, while in the samples containing TiO_2, it was 1%. When 1% (TiO_2/DEA/H_2O_2) additive was used, the Σ_{82} PCB removal efficiency was 65%, 71% and 81%, respectively. For a 10% dose, these values were found to be 45%, 86% and 85%, and for a 20% dose, the values were calculated to be 55%, 75%, and 83%, respectively. The removal efficiencies of the samples containing H_2O_2 were higher than 80%. When the average removal ratios of Dutch 7 PCBs were taken into account it was seen that PCB # 180 was the most removed congener with average removal of 83% (Figure 1). Also, the other species with high removal ratios were identified as PCB#138/163 and PCB#153. However, PCB#(28, 89/101, 118) cannot be removed by any photocatalyst. Dutch 7 PCBs removal efficiencies were calculated with several researchers and similar results were obtained within the present study (Salihoğlu et al. 2013),(Meijer et al. 2003). For example, (Salihoğlu et al. 2013) showed that the highest removal efficiencies were obtained for PCB#138/163 and PCB#153

species. When TiO_2 was used, the maximum removal efficiency for Dutch 7 PCBs were obtained by adding 20% TiO_2 (48% removal). In the case of DEA containing samples, the same maximum efficiency (57%) was reached at doses of 1% and 10% for Dutch 7 PCBs removal. In the case of H_2O_2 containing samples, the maximum Dutch 7 PCBs efficiency value were 57% and the same efficiency values were observed for all of the 1%, 10% and 20% doses. It was found that H_2O_2 was the most effective photocatalyst for the removal of Dutch 7 PCBs. In general, the removal efficiency obtained on the Σ_{82} PCB species were higher than the removal efficiency on the Dutch 7 PCBs. These results might have showed that sunlight was relatively less effective to removal of Dutch 7 PCBs than Σ_{82} PCBs. The light wavelength absorbed by the SVOCs at maximum level can vary (Fasnacht and Blough 2003; Miller and Olejnik 2001). Dutch 7 PCBs species possibly absorbed less amount sunlight than other species, and this may have caused the removal efficiencies to be relatively lower than the other species.
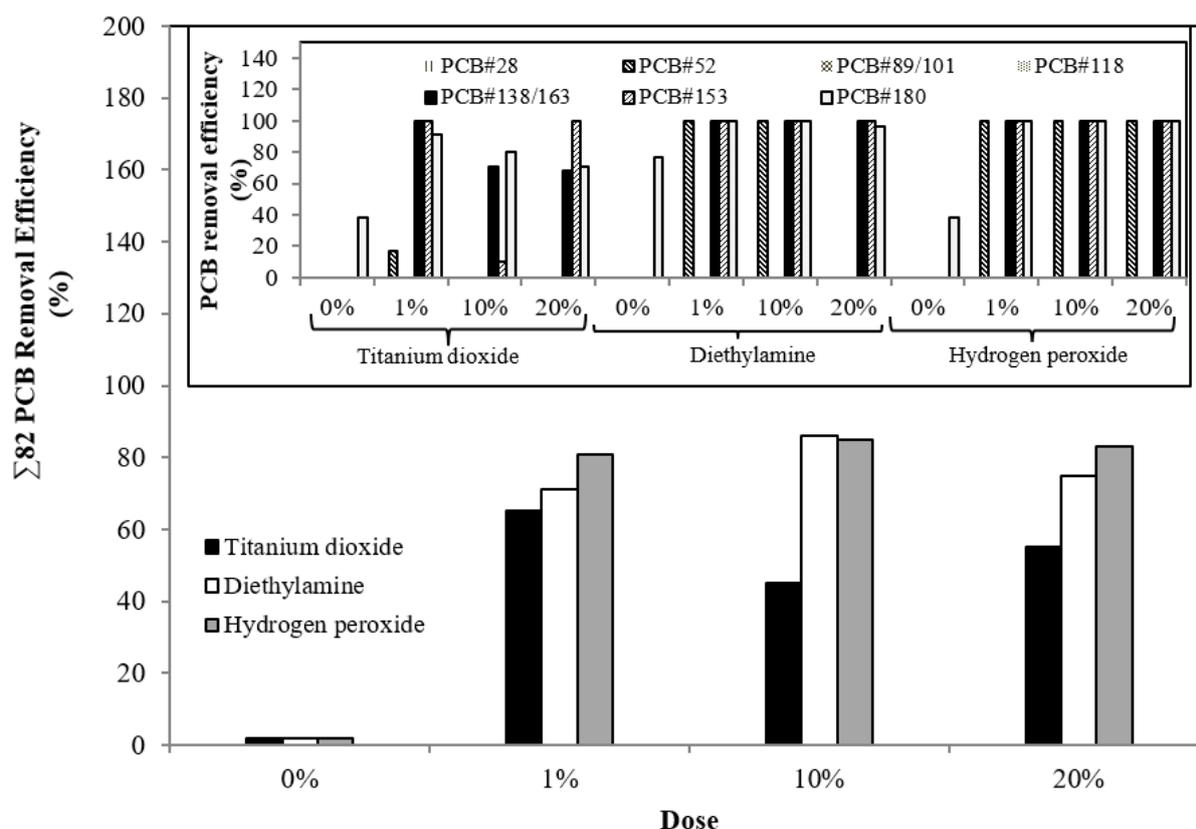

Figure 1. Total PCB removal efficiencies during ambient air applications.

Impact of TiO_2 on PCB removal

In the soil samples exposed to ambient air after the addition of 1%, 10%, and 20% TiO_2, the Σ_{82} PCB removal efficiencies were found as 65%, 45%, and 55%, respectively (Figure 1). It was determined that the PCB concentrations of the samples containing TiO_2 were reduced by more than 50%. It is known that when TiO_2 absorbs certain wavelengths of light, pairs of negative electrons (e^-) and positive holes (h^+) are generated (Pleskov 1999). The holes decompose water molecules, producing hydrogen gas and hydroxyl radicals (OH^-) (Dhol 2005, Quan et al. 2005). In addition, electrons in the transmission band react with O_2 to form superoxide anionic radicals (O_2^-) (Hoffmann et al. 1995). These radicals contribute to the degradation of organics. In this study, water present in the soil structure (12%) and O_2 absorbed on the soil surface can form radicals. It is expected that these radicals, which are not selective, are very active in the degradation of PCBs in the soil. In the study conducted by Krauss and Wilcke (2002), changes in the PCB removal amount were investigated for different soil types (silty sand, alluvial sand, etc.), and it was observed that PCB removal increased with the addition of TiO_2. In another study, river water samples containing TiO_2 exposed to sunlight for 4 hours and the removal efficiency of Arochlor 1248 was found

to be 77% (Zhang et al. 1993). In the present study, PCB removal increased as the dose of TiO_2 raised from 10% to 20%. However, despite this increase, the removal efficiency could not exceed the value found in the samples containing 1% TiO_2 (65%). Similarly, in the study conducted by Salihoglu et al. (2012) on the removal of PAHs from treatment sludge, removal efficiency reduced as the TiO_2 dose increased from 0.5% to 20%. This could be occurred because of scattered UV rays since the absorption of light might have reduced due to the increase in the TiO_2 dose (Salihoglu et al. 2012). In the studies of (Dong et al. 2010, Zhang et al. 2008), similar findings were obtained for soil.

Impact of DEA on PCB removal

The total PCB removal efficiencies in the soil sample containing 1%, 10% and 20% DEA were 71%, 86% and 75% respectively (Figure 1). It was revealed that among the three additives (TiO_2, DEA and H_2O_2), 10% DEA was the most effective one. DEA initiates chain photodegradation reactions via electron transfer (Lin et al. 2004). For electron transfer to be realized, this compound must be stimulated to free the nitrogen electrons in its structure. Lin (2004) determined that PCBs converted into anionic PCB radicals upon receiving nonbonding electrons from DEA, and meanwhile, cationic DEA radicals were formed. The PCB removal was negatively influenced with an increased DEA dose and the most effective dose was 10% (Lin et al. 2004). However, Lin (1995) reported that PCB photodegradation occurred independently from the DEA dose. In the present study, the cumulative UV-A and UV-B values measured during experiments were 198.000 Ws/m^2 and 13.090 Ws/m^2, respectively. It is thought that PCB transform into PCB^* in the presence of sunrays due to the impact of UV light. PCB^* which had a high and indecisive level of energy, reacted with DEA in the environment and that (-) loaded PCB radical are formed, which are then converted to photodegradation products (Bunce et al. 1978). The removal efficiencies were much lower in samples containing 20% DEA, might due to overdose. It is known that chemicals such as DEA perform more efficiently at doses that increase at a specific rate when they are used over than efficient dose, their effectiveness reduces (Cebe 1995, Karaca and Tasdemir 2011, Lin et al. 2004). Karaca and Tasdemir (2011) applied UV-DEA to urban sludge and determined that as the dose of DEA added to sludge increased from 0.5% to 5%, the PAH removal efficiency was reduced.

Impact of H_2O_2 on PCB removal

In all of the samples with added H_2O_2, the removal efficiencies were above 80% in the samples containing H_2O_2 (Figure 1). In a study examining the removal of phenanthrene and pyrene from Chinese soil using 0-30% H_2O_2, it was determined that the PAH concentrations were reduced by 33% after 25 hours (Dong et al. 2010). Ahmad (2011) investigated the impact of using 2-50% H_2O_2 together with phytate on the removal of PCB and maximum PCB removal efficiency was found to be 48%. In another study focusing on the addition of 4.9 M H_2O_2 to urban treatment sludge, a removal ratio of 71% was obtained for Σ_{11} PAHs (Karaca and Tasdemir 2015). Similar to DEA applications, for the samples containing H_2O_2, the most effective dose was 10%. An increase in the H_2O_2 dose did not cause a significant change in the removal efficiency. The removal efficiencies of PCB homolog groups in the soil samples containing different doses of TiO_2, DEA and H_2O_2 are provided in Figure 2. The highest PCB removal was obtained for the (4-5) chlorinated homolog group in samples containing 10% TiO_2. At all doses of TiO_2, the highest removal was observed in this group, and TiO_2 was effective the most in photodegradation reactions of (4-5) chlorinated group. This homolog group may have absorbed sunrays more easily compared with the other homolog groups, and thus, the catalysis efficiency of TiO_2 may have improved. (Weber and Sakurai 2001) determined that 3- and 4- chlorinated PCBs were removed at the maximum ratio with using TiO_2. It was thought that, during the ambient air applications, the atmospheric precipitation of (8-9) chlorinated PCB homologs may have caused removal ratios of this group to be very low (0.05%).

The (4-5) and (6-7) chlorinated homolog groups had the highest removal ratios. The impact of DEA dose on the removal of PCB homolog groups varied. The removal efficiencies increased in all homolog groups (unexpectedly, except the (2-3) chlorinated PCBs) with using DEA was not effective in the removal of light PCBs.
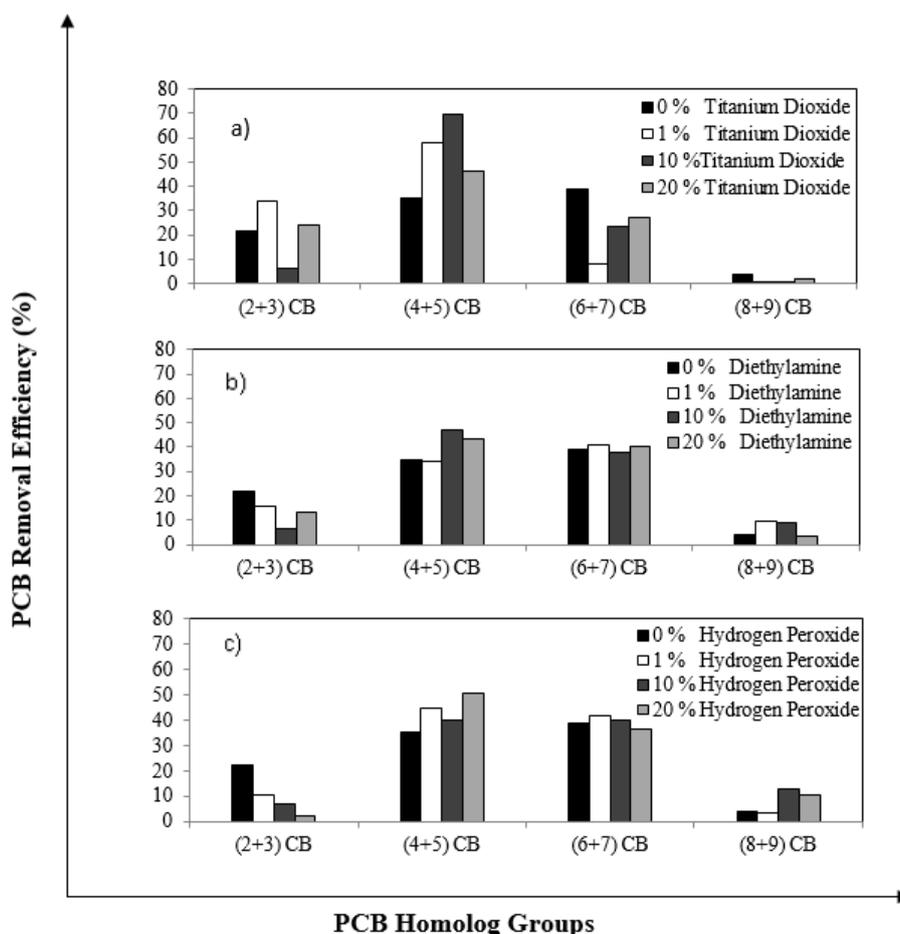
Figure 2. PCB homolog groups removal efficiencies with using additives.
a) TiO_2 b) DEA   c) H_2O_2

For the soil samples containing 1%, 10% and 20% H_2O_2, the removal efficiencies of (2-3), (4-5), (6-7) and (8-9) CB were given in Figure 2. Similar to DEA, H_2O_2 caused a reduction in the removal ratios of the (2-3) chlorinated homolog group. Considering that the volatility of the (2-3) chlorinated homolog group is relatively high, a higher level of removal would be expected in the present study due to evaporation effects. However, the opposite result was obtained, and it was thought that highly chlorinated PCBs converted to low chlorinated PCBs during photodegradation. Similarly, previous studies determined that SVOCs such as heavy PAHs converted into lighter ones during photodegradation (Guieysse et al. 2004, Ireland et al. 1995, Karaca et al. 2014). The concentrations of the PCB homolog groups varied as the dose of H_2O_2 increased (Figure 2). The removal efficiencies of homolog groups with (4-5) CB and (8-9) CB increased at H_2O_2 doses of 1% to 20% but decreased at a dose of 10%. In analogs with (6-7) CB, as the dose increased, a certain reduction was seen in removal efficiencies.   Similar to the TiO_2 and DEA applications, it was observed that for the photodegradation reactions occurring in the presence of H_2O_2, the (4-5) PCB group had highest removal efficiency. For this homolog group, the removal efficiencies varied between 45-51%.

CONCLUSIONS

In this study, the removal of PCBs by using various additives (TiO_2, DEA, and H_2O_2) in the ambient air conditions was investigated. The main results were as follows:

- It was determined that sunlight was not effective in the degradation of PCBs in soil without the use of additives. In the soil samples exposed to ambient air conditions without additives, only 2% of the Σ_{82} PCBs were removed.
- With the addition of 1%, 10% and 20% TiO_2, the Σ_{82} PCB concentration reduced by 65%, 45% and 55%, respectively. It was determined that the most appropriate TiO_2 dose was 1%, and an increase in the dose may have cause to scattering effect and reduced the PCB removal efficiency.
- In the DEA and H_2O_2 applications, it was determined that the most effective dose for PCB removal was 10%, and it was not required to use additives at higher ratios.
- It was concluded that, the most effective additive for PCB removal was DEA (10%) in ambient air applications. The Σ_{82} PCB concentrations were reduced by 86%.
- In all applications, it was observed that the (4-5) chlorinated homolog group was effectively removed (maximum 70%), and the (8-9) chlorinated group had the minimum removal ratios.

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