



Photochemical of Polychlorinated biphenyl by the photolysis and solvent

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ABSTRACT: Polychlorinated biphenyls (PCBs) are one group of persistent organic pollutants (POPs) that are of international concern because of global distribution, persistence, and toxicity. Removal of these compounds from the environment remains a very difficult challenge because the compounds are highly hydrophobic and have very low solubility in water. The photochemical reactor was of annular geometry with a cylindrical low-pressure mercury lamp. The whole Lamp was immersed in a reactor thermostat controlling the temperature at 32 ± 2 °C. The Polychlorinated biphenyls (PCBs) were analyzed by GC/ECD. The degradation of PCBs in terms of one, two and three lamp was 91.9%, 92.7% and 93% respectively. The degradation of PCBs in terms of use of 10% and 20% of total volume of solution of H₂O₂ were 88.8% and 93% respectively. The degradation of PCBs in terms of ratio to ethanol with oil transformer in 1:1, 2:1 and 3:1 was 83.4%, 92.5% and 93% respectively. The experiments show that UVC-photolysis of H₂O₂ leads to a degradation efficiency of PCBs in the presence of ethanol. @ JASEM

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Polychlorinated biphenyls (PCBs) are one group of persistent organic pollutants (POPs) that are of international concern because of global distribution, persistence, and toxicity. Removal of these compounds from the environment remains a very difficult challenge because the compounds are highly hydrophobic and have very low solubility in water (Fang et al. 2008). Polychlorinated biphenyls (PCBs) were produced from 1930s, with particularly large volume to 1970s (Wong et al. 2006), producing a complex mixture containing 60–90 congeners (Wenhai et al. 2005; Borja et al. 2005). They were used in a wide range of industrial applications because of their excellent physical and chemical properties. Polychlorinated biphenyls (PCBs) are toxic, persistent, bio-accumulate and pose a risk of causing adverse effects to human health and the environment. For different social, technical and economic reasons, significant quantities of PCBs contaminated transformer oil are still in use or in storage (Manzano et al. 2004; Xitao et al. 2006). For several decades PCBs were used extensively in a wide range of industrial applications such as: oil in transformers, dielectrics in capacitors, hydraulic fluids in hydraulic tools and equipment and heat exchange liquids (Wenhai et al. 2005; Borja et al. 2005).

Most of the dechlorinating processes for wastes containing PCBs were carried out in various organic solvents (2-9). In the case of PCBs contaminated transformer oil, from the practical point of view, dechlorinating PCBs directly in oil is a suitable disposal method. Such process leads to easily reusing the transformer oil and avoids using plenty of organic solvents, which are usually volatile and toxic. However, waste transformer oil is complex, viscous and is usually contaminated by other metals and impurities. It is difficult to dechlorinate PCBs in transformer oil directly. Little work is done to study the dechlorination process in oil transformer. For the aim of practical application, more information about dechlorination of PCBs directly in transformer oil is needed to know (2-9).

Incineration is the most commonly used technology to treat wastes with high concentrations of PCBs, particularly dielectric oils, and this achieves an elimination of almost 100%. But in spite of this, incineration also presents environmental risks (dioxins and benzofurans) and is limited by the high costs of handling, transport and elimination of the final contaminated material (Wenhai et al. 2005; Borja et al. 2005; Manzano et al. 2004; Chang et al. 2003; Shih et al. 2008; Xitao et al. 2006). Alternative treatments under development for this type of residue are: chemical reaction with an alkaline hydroxide in polyethylene glycol; supercritical and wet oxidation; adsorption onto activated carbon-regeneration; and Fenton oxidation (3-11).

With respect to photochemical treatments, the main concern of this paper, a distinction must be made with respect to irradiation, solvent and oxidizing agent employed. When sources that emit at wavelengths above 300nm are employed, such as sunlight, the absorption of light by the polychlorinated biphenyls is very small. In such case, in order that a reaction take place (sensitized photolysis), photosensitizers must be added (3-14). If ultraviolet light is used as the source of irradiation, reactions of the direct photolysis type take place, since the PCBs absorb considerably in this region of the spectrum. This study was conducted to determine the effect of UV-C, hydrogen peroxide and solvent on the photodegradation of PCBs including PCB in transformer oil.

MATERIAL AND METHODS

Oil transformers were obtained from Regional Electric Company in Sari. Ethanol (C₂H₅OH), Acetone (CH₃COCH₃), Sodium Hydroxide (NaOH) (all p.a. quality, Merck) and hydrogen peroxide (H₂O₂, Merck) were used without further purification. The photochemical reactor was of annular geometry (500 ml volume) with a cylindrical low-pressure mercury lamp (UV-C Cathodeon TUV 6WE) emitting at 254 nm. The radiant power emitted by the lamp was 6 W. The whole Lamp was immersed in a reactor thermostat controlling the temperature at 32 ± 2 °C. The pH of the samples and the temperature of the solution inside the photoreactor were continuously monitored. Transformer oil was dissolved in ethanol to dilution and increases its aqueous solubility and donor of hydroxyl group. Volumes of ethanol and transformer oil (1:1, 2:1 and 3:1) were in various samples. Concentration of acetone that acted as a sensitizer was used to ensure the enhancement of PCBs photodegradation. The reaction mixture inside the cell was continuously stirred with a magnetic bar. The samples contained the appropriate volume of oil contaminated by PCBs, ethanol and sodium hydroxide solution (0.2 N) for each assay and the photosensitizer, acetone. The adjustment of the pH of the solution was done using NaOH solution. For the effect of initial PCB concentrations, H₂O₂ concentrations used were based on the optimum amount obtained, maintaining the PCB/hydrogen peroxide ratio in the solution in all the experimental runs. The experiments were performed in triplicate and the results are presented as mean concentrations. The controls were treated similarly but not irradiated, in order to determine the losses not due to the photochemical reaction. The selected exposure times were 2, 4 and 6 h.

The PCBs were analyzed by GC/ECD (Perkin Elmer Autosystem HRGC, Norwalk, CT, USA) with hexane as internal standard. The identification of the resulting photoproducts was performed at the Laboratory Services of department of environment of Iran by GC/MAS. Samples were taken at varying

time (2, 4 and 6 hour) intervals and analyzed immediately or stored at 4°C up to 3–5 h before analysis. For quality control, the experiments were conducted in three replicates. To prevent from exposure while exposed to irradiation, samples covered with aluminium foil were exposed to UV lamps. Samples without the catalyst were also used to investigate the effect of direct photodegradation of PCBs.

RESULTS AND DISCUSSION

Identified PCBs in PCB transformer oil is included PCB101, PCB138, PCB153, PCB180, PCB194, and PCB1260. The initial concentration of PCBs is showed in table 1. Also, the table 1 is showed percent of degradation of PCBs without solvent and H₂O₂.

Table 1: initial concentration of PCBs in PCB transformer oil

PCB	PCB101	PCB138	PCB153	PCB180	PCB194	PCB1260
Value (µg/L)	1190	2500	2965	2920	2130	16240
% degradation of PCBs (blank sample-without ethanol and H ₂ O ₂)	2	0.5	0.04	0.0	1.2	0.0

Experimental conditions: pH= 7±0.5, Temperature= 34 ± 1.5, exposure time= 6 hour

Table 2 showed the effect of intensity of lamp in similar times in samples. The degradation of total PCBs in terms of one, two and three lamp was 91.9%, 92.7% and 93% respectively. Results showed that the photolysis rate was very high during the first one or two time point, which was then slow down and level off when the irradiation proceed. This indicated that

the reactor was highly efficient in dechlorinating the congeners tested, and optimising the time for photolysis reduced the reaction time and therefore the main cost of the treatment, i.e. energy cost of producing UV radiation can be minimised (Wong et al. 2006; Manzano et al. 2004; Chang et al. 2003; Shih et al. 2008; Xitao et al. 2006).

Table 2: Effect of UV intensity on PCBs degradation efficiency (%) of photolysis

PCBs Lamp	Exposure Time (hour)	PCB101	PCB138	PCB153	PCB180	PCB194	PCB1260	Mean
1 Lamp	2	86.87	86.53	89.71	88.63	91.43	84.12	87.8
	4	88.89	87.33	91.86	88.47	91.49	85.41	88.9
	6	89.71	91.57	92.76	92.46	96.25	89.03	91.9
2 Lamp	2	71.37	67.09	66.01	73.23	73.85	61.88	69
	4	92.5	91	94.58	93.58	94.92	92.69	93
	6	93.62	91.58	95.19	92.25	92.07	92.06	92.7
3 Lamp	2	91.22	91.53	93.87	92.43	96.01	90.31	92.5
	4	91.36	92.02	93.68	92.88	96.43	90.06	92.7
	6	99.76	95.64	97.82	93.60	82.16	88.83	93

Experimental conditions: Volumes of ethanol and transformer oil (3:1), pH= 7±0.5, Temperature= 34 ± 1.5

UV lamps provide most light energy in a single line spectrum such as 254 nm that can be strongly absorbed by most xenobiotics including PCBs (3). As a result, UV lamps are the most commonly chosen light source on our study. Table 2 showed the effect of changing UV intensity on the degradation efficiency of PCB congeners. In general the degradation efficiency increase with increasing UV intensity, and the degradation efficiency tended to plateau from one lamp 6W to three lamps 6W. For direct photolysis, photons need to be absorbed and the adsorbed radiation must be capable of degrading the compound (Wong et al. 2006; Manzano et al. 2004; Chang et al. 2003; Shih et al. 2008; Xitao et al. 2006). UV is the driving force of photolysis reaction, which involved absorbing the UV energy to excite the PCB molecule followed by cleavage of C-Cl bond. As a result, increasing the UV intensity will provide more

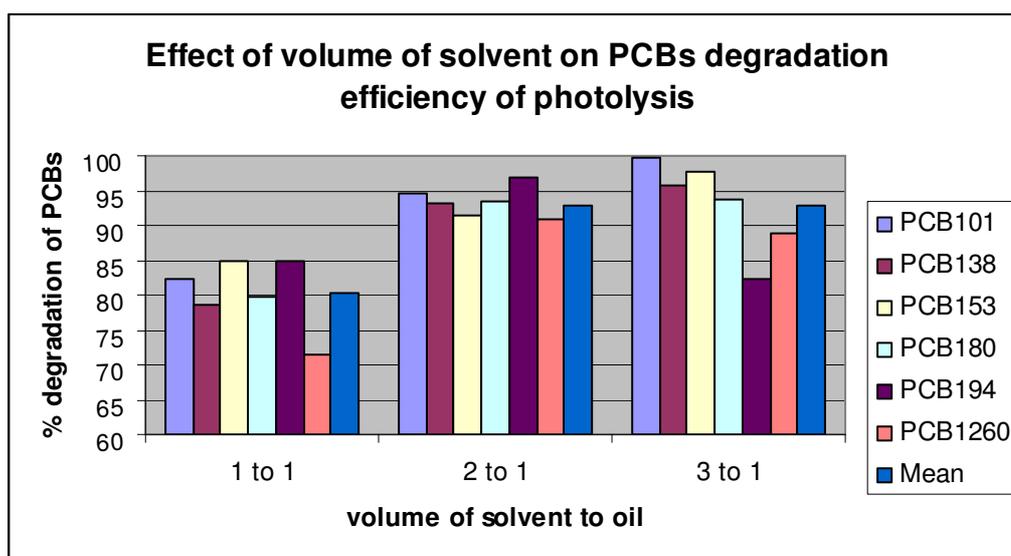
photon and so increase the degradation efficiency. However, if we treat UV photon as a kind of particle but not electromagnetic wave, the dechlorination reaction now has two reactants: PCB molecule and photon. When the concentration of one reactant, in this case photon, is in excess, the reaction rate will become dependant on the concentration of another reactant only, i.e. PCB in the experiment. Since the concentration of PCB is constant, more UV will not further increase the rate and hence the degradation efficiency will plateau. In this reaction mechanism, PCB absorbed photon, activated and dechlorinated by homolysis. The radicals then abstract a hydrogen atom from the solvent to form dechlorinated product. The solvent radicals start a reaction cycle to further dechlorination more PCB molecules (Borja et al. 2005). Then the dechlorination of PCB proceeds in stepwise reductive dechlorination (Chang et al. 2003).

In general, the effect of the lamp power is expected to be straightforward. Since the major mechanism for generation of hydroxyl radical is photolysis of hydrogen peroxide, increasing the power of the UV lamp should increase the generation rate of hydroxyl radical and thus the oxidation of the PCBs (Wong et al. 2006; Manzano et al. 2004; Chang et al. 2003; Shih et al. 2008; Xitao et al. 2006; Yao et al. 2000).

Figure 1 showed the effect of solvent, i.e. ethanol. The degradation of PCBs in terms of ratio solvent

with oil transformer in 1:1, 2:1 and 3:1 was 83.4%, 92.5% and 93% respectively. Because all chlorobiphenyls are poorly soluble in water, early work on PCB photolysis was carried out in alkanes and alcohols. The many organic solvents are employed in previous studies. Solvents such as hexane, isooctane, 2-propanol and methanol are used by some researchers (Wong and Wong 2006; Manzano et al. 2005; Chang et al. 2003; ATSDR 2000; Lin et al. 2004).

Figure 1: Effect of dilution of ethanol on PCBs degradation (%) of photolysis



Experimental conditions: Volumes of ethanol and transformer oil (1:1, 2:1, 3:1), pH= 7±0.5, Temperature= 34 ± 1.5, exposure time= 6 hour

The overall photochemistry in both organic and aqueous media is predominantly dechlorination, but, depending on the solvent used, some solvent derivatives can also be found (Xitao and Gang 2006; Lin et al. 2006; Yao et al. 2000; Lin et al. 2004; Xue et al. 2008). Photochemical decomposition using alkaline isopropyl alcohol would not be useful in aqueous media because water inhibits the reaction by protonating the reactive radical. However, there were a few reports found that employ ethanol. It was reasonable to predict that the performance of ethanol should be in between or similar to others solvent. The some of solvents, for example, hexane and isooctane is highly flammable, and the photolysis may take long time for high PCB concentration, fire hazard is of concern. However, the photoreaction rate of PCB was found to be faster in hydroxylic solvents than non-polar solvents (Yao et al. 2000).

In general, the effect of the ethanol volume is expected to be straightforward. Since the major mechanism for generation of hydroxyl radical is photolysis of hydrogen peroxide, increasing the concentration of ethanol should increase the generation rate of hydroxyl radical and thus the oxidation of the PCBs.

Table 3 and figure 2 shows the effect of initial H₂O₂ concentration on the degradation of PCBs with the use of UV/H₂O₂ process. The degradation of PCBs in terms of use of 10% and 20% of total volume in samples of H₂O₂ were 88.8% and 93% respectively. As expected, the degradation rate of PCBs increased with increasing the concentration of H₂O₂ added. This can be explained by the effect of the additionally produced OH[•] radicals (Katsumata et al. 2006).

Table 3: Effect of Hydrogen Peroxide on PCBs degradation (%) of photolysis

PCBs	Time (hour)	PC B1	PCB 138	PCB 153	PCB 180	PCB 194	PCB 1260	Mean

)	01						
10 % H ₂ O ₂	2	67.7	60.41	69.66	60.08	82.16	37.18	62.9
	4	75.6	87.62	91.95	87.57	92.11	80.56	85.9
	6	86.8	87.64	91.97	85.11	92.43	78.38	88.8
20 % H ₂ O ₂	2	91.2	91.53	93.87	92.43	96.01	90.31	92.5
	4	91.6	92.02	93.68	92.88	96.43	90.06	92.7
	6	99.7	95.64	97.82	93.60	82.16	88.83	93

Experimental conditions: Volumes of ethanol and transformer oil (3:1), pH= 7±0.5, Temperature= 34 ± 1.5

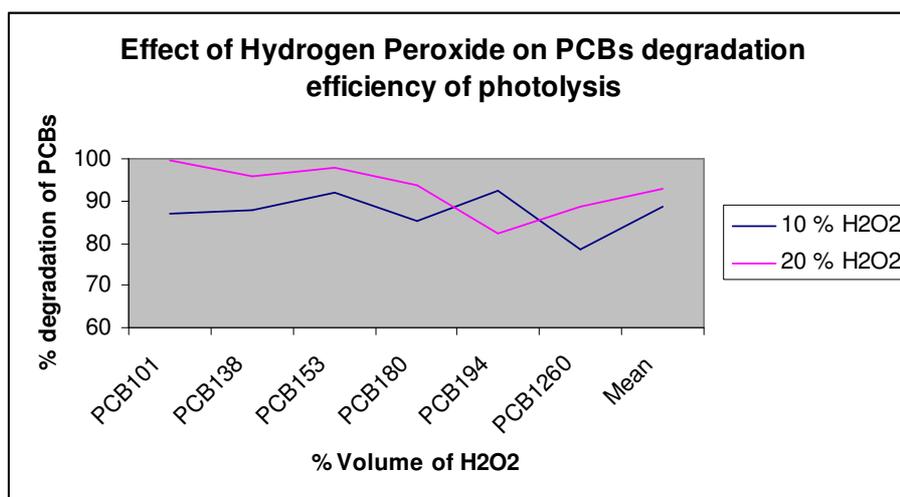


Figure 2: Effect of Hydrogen Peroxide on PCBs degradation (%) of photolysis: *Experimental conditions:* Volumes of ethanol and transformer oil (1:1, 2:1, 3:1), pH= 7±0.5, Temperature= 34 ± 1.5, exposure time= 6 hour

Results showed that 254-nm irradiation alone cannot be used as an effective procedure for the removal of PCBs. Some studies indicated that the removal efficiency of PCBs by UV radiation could be raised by the addition of H₂O₂. When H₂O₂ is added, the dominant mechanism of PCBs destruction becomes hydroxyl radical mediated advanced oxidation, and the highly reactive OH radical species produced in the process are expected to quickly react with PCBs. The hydroxyl radical is an extremely reactive and nonselective oxidant and, thus, when produced in sufficient quantities, can lead to complete oxidation of organic compounds to carbon dioxide, water, and inorganic ions (Xue et al. 2005). The OH^{*} radical may oxidize substrate, but because of its high reactivity it also may react with a variety of other substances commonly found in PCBs.

The hydrogen peroxide dose is very important parameter for the efficiency of the treatment process and the economic desirability. In the UV/H₂O₂ process, the photolysis of hydrogen peroxide is the major mechanism generating hydroxyl radicals. Therefore it is logical to assume that increasing the

dose of hydrogen peroxide would increase the transient-state concentration of hydrogen peroxide. This is not the case though, because hydrogen peroxide acts as a hydroxyl radical scavenger too (Lin et al. 2006; Yao et al. 2000; Lin et al. 2004; Xue et al. 2008; Katsumata et al. 2006). It is obvious that at low initial hydrogen peroxide concentrations, increasing the dose significantly increase the degradation rate of the PCBs. At higher concentration, the effect of increasing the dose is negligible. This is a reasonable result since the hydroxyl radical production is limited from the photolysis rate (when hydrogen peroxide absorbs all the available light). Increasing the hydrogen peroxide dose further from that point acts only to increase the hydroxyl radical scavenging from hydrogen peroxide.

Conclusion: Our experiments show that UVC-photolysis of H₂O₂ leads to a degradation efficiency of PCBs in the presence of ethanol, therefore indicating that the intermediates formed after ethanol oxidation are able to initiate PCBs degradation.

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