

Degradation of Transformer Oil (PCB Compounds) by Microwave Radiation, Ethanol Solvent, Hydrogen Peroxide and Dioxide Titanium for Reducing Environmental Hazards

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ABSTRACT

Background: Poly chlorinated biphenyls (PCBs) are a class of chlorinated organic chemicals that do not easily degrade in the environment. This study was conducted to determine the effect of microwave rays, hydrogen peroxide, dioxide titanium and ethanol solvent on the degradation of PCBs.

Methods: A 900w domestic MW oven with a fixed frequency of 2450 MHZ was used to provide MW irradiation. Ray powers were used in 540, 720, and 900w. A hole was made on the top portion of the oven and a Pyrex vessel reactor (250ml volume) was connected to condensing system with a Pyrex tube connector. The PCBs were analyzed by GC-ECD.

Results: The degradation of total PCBs was 54.62%, 79.71%, and 95.76% in terms of their ratio to solvent with transformer oil at 1:1, 2:1, and 3:1, respectively. The degradation of total PCBs was 84.27%, 89.18%, and 96.1% when using 540, 720, and 900W microwave radiation, respectively. The degradation of total PCB_s was 70.72%, 93.02%, 94.16, 95.23% and 96.1% when not using H₂O₂/ TiO₂ and using 20% H₂O₂ and 0.05, 0.1, 0.15, and 0.2g TiO₂, respectively.

Conclusion: In the present study, the optimum conditions to decompose PCBs efficiently included 50 ml volume of ratio to solvent with transformer oil (3:1), sodium hydroxide solution (0.2N) 1 cc, use of 20% hydrogen peroxide of total volume of samples, dioxide titanium (0.2g), and irradiation for 9 minutes. Under these optimum conditions, efficiency of PCBs decomposition increased.

Keywords: Degradation, Microwave, Pcb_s, TiO₂.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are a family of compounds produced commercially by the direct chlorination of biphenyl so that production of 209 different PCB congeners is possible (1). Because of their excellent flame resistance, electrical properties, and chemical stability, PCBs have been used worldwide

as heat-transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame retardants, organic diluents, and dielectric fluids (2-5). Such an extensive application of these chemically and thermally stable compounds has resulted in widespread ecological contamination (2). Due to potential adverse human health and environmental effects, the use of PCBs has

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been ceased and a way out for existing PCB contamination has become of substantial interest (3,6). PCBs are principally being destroyed by incineration. This achieves an elimination of almost 100% (7,8).

Incineration, however, often produces more toxic compounds if it is not carefully controlled. Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) have been detected in combustion of PCBs (9). Now it is more apt to accept non-combustion technologies for treatment of PCBs containing wastes. Other proposed methods for destruction of PCBs include wet air oxidation, biodegradation, reaction with superoxide, photodechlorination, sodium metal-promoted dehalogenation, electrolytic reduction, and dechlorination with zero-valent iron (3-5,10-13). In recent years, microwave irradiation has been applied for decomposition or dechlorination of chlorinated organic pollutants. In this field, a series of pioneer studies were carried out by Abramovitch *et al.*, (1998-1999) that adopted microwave irradiation for remediation of PCBs polluted soil. The results have been promising (14,15).

Subsequently, Raquel *et al.*, (2002) investigated microwave decomposition of lindane supported on modified sepiolites. They found that trichlorobenzene and pentachlorocyclohexene are made from NaOH-modified sepiolite by short time microwave irradiation (16). The majority of dechlorinating processes for wastes containing PCBs is carried out in various organic solvents (2). In the dechlorination process, the role of NaOH, on the one hand, is to activate chlorinated compounds, and, on the other hand, is to neutralize HCl produced during dechlorination (17). We believe that microwave heating can be employed as energy input to take the place of conventional heating to accelerate the thermal reaction (18).

MATERIALS AND METHODS

This experimental study was carried out in the laboratory of the Department of Occupational and Environmental Health of Tarbiat Modares University, Tehran, Iran.

Reagents and Materials

Grain TiO_2 was GT01 (HSD company, china), the particle diameter of GT01 was 180-250 μm which was small enough for suspension, yet large enough for settlement by gravity. The BET surface area of GT01 was 194.4 m^2/g with density of 900 kg/m^3 . Hydrogen peroxide, ethanol solvent, and sodium hydroxide (all p. ap quality, Merck) were used without any purification prior to use. Oil transformers were obtained from the regional electric company.

Apparatus

The experimental apparatus used in this study was a 900w domestic MW oven (380mm×380mm×300mm, made in LG Company) that was used to provide microwave irradiation, which had been modified by an aperture made on the top of the oven for the communication pipe to get through. A Pyrex flat bottom reactor (250ml) was installed in the microwave oven, with which a 600mm long water reflux condenser was connected through a communication pipe. An aluminum tube fixed in the aperture was used to eliminate MW leaking. To limit leakage of the safe stray, MW power density was kept below 0.5 mw/cm^2 at 2450 MHz measured at 200mm distance from the aperture. Temperature in the reactor was measured by quickly stopping the MW oven which was found to be less than 78°C.

Methods

The four reactants of hydrothermal reaction, ethanol solvent, NaOH, TiO_2 , and H_2O_2 , together with the transformer oil were put into the Pyrex reactor and were heated by microwave irradiation. The top of the reactor outside the microwave oven was connected to a condensing system.

Hexane and deionized water were used for washing the reactor and other vessels. After microwave irradiation, the materials in the reactor were combined. The combined materials were centrifuged to obtain organic and water phase. Volumes of ethanol and transformer oil were 1:1, 2:1, and 3:1 in various samples. Rapid rise in temperature of the contents of the reactor via microwave radiation was aimed to control the reactor during the reactor condition, whereas the radiation was discontinuous. Hence, after several trials, radiation was continued for 10 seconds with intervals of 30, 40, and 50 seconds between radiation stages for the selected exposure times of 3, 6, and 9 minutes, respectively. Adjustment of pH of the solution was performed for each assay using NaOH solution. H₂O₂ concentrations and TiO₂ quantities were used based on optimum amount obtained from initial PCB concentrations maintaining PCB/hydrogen peroxide and dioxide titanium ratio in the solution in all experimental runs. The reactor was on the turn section of the microwave for the same exposures.

Analysis

The organic phase was diluted with hexane. Decachlorobiphenyl was added as the internal standard. The PCBs were analyzed by GC/ECD method (Trace GC ultra USA). Data were analyzed by repeated measures ANOVA and t-test using SPSS software version 16.0. P-values less than 0.05 were considered significant. Analysis of resulting byproducts was performed by GC/MAS at the laboratory of Kimia Shengerf Pars Company, Iran. The PH of the samples was periodically controlled with a Methrom-Herisau pHmeter (E512). The samples were taken at varying time (3, 6 and 9 minutes) intervals and were analyzed immediately or were stored at 4°C up to 3-5 hours before analysis. For quality control, the experiments were conducted in three replicates. The capillary column used

was a DB-5 and the carrier gas was helium. The capillary column (narrow-bore) 30m×0.32mm ID fused silica capillary column chemically boned with 5 percent phenyl methyl and 0.25µm film thickness. Helium was used as the carrier gas with a flow rate of 1.3ml min⁻¹ and N₂ was used as make-up gas with a flow rate of 60 ml min⁻¹. The injector and detector temperatures were set at 280°C and 300°C, respectively. A split-splitless injector in the splitless mode was used. The column temperature was programmed as follows: 50°C (30Sc), 12°C min⁻¹ to 130°C and 5°C min⁻¹ to 280°C and 5 min hold.

RESULTS

Identified PCBs in PCB transformer oil included PCB138 and PCB180. Initial concentrations of PCBs in addition to the percentage of degradation of PCBs without solvent, H₂O₂, and TiO₂ are demonstrated in Table 1.

Table 2 shows the effects of the power of microwave in comparable times on the samples. The degradation of total PCBs in terms of 540, 720, and 900w was 84.27%, 89.18%, and 96.1% respectively.

Table 3 and Figure 1 show the effects of volume of solvent, i.e. ethanol on PCBs degradation. The degradation of total PCBs in terms of ratio solvent to oil transformer in 1:1, 2:1 and 3:1 was 54.62%, 79.71%, and 95.76%.

Table 1. Initial concentrations of PCBs in PCB transformer oil

PCB	PCB138	PCB180
Value (µg/L)	2492	3333
% degradation of PCBs (blank sample-without ethanol, H ₂ O ₂ and TiO ₂)	1.6	2.25

Experimental conditions: pH= 7±0.5, temperature= 76 ± 1.5°C, exposure time= 9min, power=900w

Table 2. Effect of MW power on PCBs degradation efficiency (%)

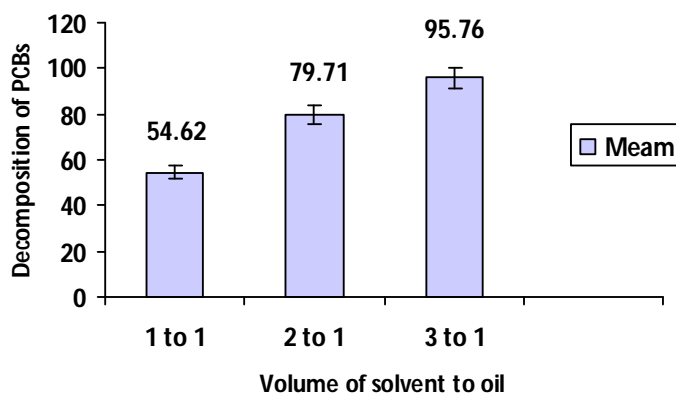
Power	PCBs Exposure Time (min)	PCB138	PCB180	Mean
540w	3	81.71	81.48	81.59
	6	83.23	82.59	82.91
	9	84.75	83.80	84.27
720w	3	87.39	86.24	86.81
	6	88.19	87.02	87.60
	9	89.56	88.80	89.18
900w	3	94.83	93.28	94.05
	6	95.75	94.48	95.11
	9	96.62	95.58	96.1

Experimental conditions: Volume of ethanol and transformer oil (3:1), pH= 7±0.5, Temperature in 540w= 37 ± 1.5°C (3min), 41 ± 1.5°C (6min), and 46 ± 1.5°C (9min), in 720w = 51 ± 1.5°C (3min), 55 ± 1.5°C (6min), and 60 ± 1.5°C (9min), in 900w = 65 ± 1.5°C (3min), 69 ± 1.5°C (6min), and 74 ± 1.5°C (9min)

Table 3. Effect of volume of solvent on PCBs degradation efficiency (%)

PCBs	PCB138	PCB180	Mean
Volume of solvent to oil			
1:1	54.47	54.78	54.62
2:1	79.53	79.89	79.71
3:1	95.18	96.34	95.76

Experimental conditions: pH= 7±0.5, Temperature= 74 ± 1.5°C, exposure time= 9 min, power=900w

**Figure 1.** Effect of dilution of ethanol on PCBs degradation (%).

Experimental conditions: Volume of ethanol and transformer oil (1:1, 2:1 and 3:1), pH= 7±0.5, temperature= 74 ± 1.5°C, exposure time= 9 min, power=900w

Table 4 and Figure 2 show the effects of H₂O₂ concentrations on the degradation of PCBs during MW/H₂O₂ process. Degradation of PCBs in terms of

using 10% and 20% H₂O₂ of total volume in samples was 83.07% and 87.71%, respectively. Table 5 shows the effects of degradation of PCBs in terms of not using

H₂O₂/TiO₂ or using 10% and 20% H₂O₂ with 0.05, 0.1, 0.15, and 0.2 g TiO₂. Degradation of total PCBs in terms of not using of H₂O₂/TiO₂, using 10% H₂O₂, and 0.05, 0.1, 0.15, and 0.2 g TiO₂ was 73.39% , 89.03% , 89.93% , 91.53% and 92.03% ,

respectively. Degradation of total PCBs in terms of not using of H₂O₂/TiO₂, using 20% H₂O₂ and 0.05, 0.1, 0.15, and 0.2 g TiO₂ was 73.39% , 93.02% , 94.16% , 95.23% , and 96.1% .

Table 4. Effect of hydrogen peroxide on PCBs degradation (%)

Peroxide Hydrogen	PCBs	Time (min)	PCBs		
			PCB138	PCB180	Mean
10 % H ₂ O ₂		3	80.74	80.95	80.84
		6	82.43	81.53	81.98
		9	82.94	83.21	83.07
20 % H ₂ O ₂		3	84.51	85.88	85.19
		6	86.29	87.16	86.72
		9	87.80	87.62	87.71

Experimental conditions: Volumes of ethanol and transformer oil (3:1), pH= 7±0.5, temperature = 65 ± 1.5°C (3min), 69 ± 1.5°C (6min) and 74 ± 1.5°C (9min), power = 900w

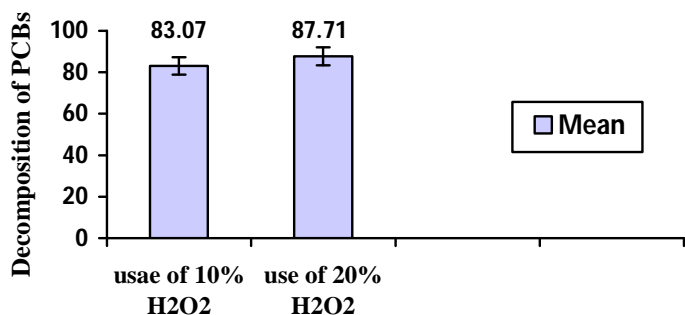


Figure 2. Effect of hydrogen peroxide on PCBs degradation %

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Experimental conditions: Volume of ethanol and transformer oil (3:1), pH= 7±0.5, temperature= 74 ± 1.5°C, exposure time= 9 min, power=900w

Table 5. Effect of hydrogen peroxide and dioxide titanium on PCBs degradation (%)

H ₂ O ₂ /TiO ₂	PCBs		
	PCB138	PCB180	Mean
Not using of H ₂ O ₂ /TiO ₂	74.15	72.63	73.39
10% H ₂ O ₂ +0.05 g TiO ₂	89.56	88.51	89.03
10% H ₂ O ₂ +0.1 g TiO ₂	89.88	89.98	89.93
10% H ₂ O ₂ +0.15 g TiO ₂	91.49	91.57	91.53
10% H ₂ O ₂ +0.2 g TiO ₂	91.81	92.26	92.03
20% H ₂ O ₂ +0.05 g TiO ₂	93.41	92.63	93.02
20% H ₂ O ₂ +0.1 g TiO ₂	94.22	94.10	94.16
20% H ₂ O ₂ +0.15 g TiO ₂	95.18	95.28	95.23
20% H ₂ O ₂ +0.2 g TiO ₂	96.62	95.58	96.1

Experimental conditions: Volume of ethanol and transformer oil (3:1), pH= 7±0.5, temperature= 74 ± 1.5°C, exposure time= 9 min, power=900w

DISCUSSION

The belief of heating with microwave energy is based on the direct effect of microwaves on molecules by ionic conduction and dipole rotation. Polar molecules and ionic solutions strongly absorb microwave energy because they have a permanent dipole moment that is affected by microwaves. Microwave energy absorption in a solution can occur by any of these three mechanisms. Firstly, the sample can be immersed in a single solvent or a mixture of solvents that strongly absorbs microwave energy. Secondly, the sample can be extracted in a combined solvent containing solvents with both high and low dielectric losses mixed in various proportions. Thirdly, a sample with a high dielectric loss can be extracted with a microwave transparent solvent (19).

Extraction and partitioning of solutes can occur by any combination of these three microwave assisted extraction (MAE) modes. Therefore, in order to enhance the absorption of microwave energy, solvents with a high dielectric constant, such as ethanol, are preferred. In the present study, the optimum solvent volume and irradiation time were established under different experimental conditions. Because all chlorobiphenyls are poorly soluble in water, early studies on PCB degradation were carried out in alkanes and alcohols. Many organic solvents were employed in previous studies. Solvents, such as hexane, isooctane, 2-propanol, and methanol, have been used by some researchers (2,4,10). Overall, photochemistry in both organic and aqueous media is predominantly dechlorination; nevertheless, depending on the solvent used, some solvent derivatives can also be found (13,20-23). Photochemical decomposition using alkaline isopropyl alcohol would not be useful in aqueous media because water inhibits the reaction by protonating the reactive radicals. However, there are few

reports that have employed ethanol for this purpose. It is reasonable to predict that the performance of ethanol is similar to other solvents. Some solvents, e.g. hexane and isooctane, are highly flammable. When degradation takes a long time for high PCB concentrations, fire hazard will be of concern. However, reaction rate of PCB was found to be faster in hydroxylic solvents than non-polar solvents (21). Ethanol solution was used as the intermediate solvent to absorb thermal energy of microwave irradiation and spread it.

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

The microwave oven used in the present study was a modified one; the power levels used here were discontinuous and only timed mark/space ratio could be controlled. Three power levels (540 w, 720 w, and 900 w) were investigated. Other parameters were as follow: 10% and 20% concentration of H₂O₂ (0.058 mole and 0.116 mole), 0.05, 0.1, 0.15, and 0.2g TiO₂, NaOH 0.2 N (1^{cc}), ethanol solvent ratio to transformer oil 1:1(25 cc ethanol and 25 cc oil), 2:1(33.33 cc ethanol and 16.67 cc oil) and 3:1 (37.5 cc ethanol and 12.5 cc oil) and 3, 6, and 9 minutes microwave irradiation time.

Six reactants participated in both microwave thermal reaction and dechlorination process, so the amounts of the reactants added were crucial. Their effects were investigated by adding 0.116 mol of H₂O₂, 0.2g TiO₂, 900w power, NaOH 1 cc over a 9-minute exposure time and 3:1 ratio to solvent while high oil efficiency of dechlorination was obtained. After 9 minutes of microwave irradiation, almost all PCB congeners were degraded in the simulative transformer oil. HCl

produced during dechlorination of PCBs was neutralized by NaOH. Therefore, the experiments were designed to investigate the effects of reduced amounts of reactants on dechlorination. Dechlorination efficiency was calculated based on the chlorine ions produced.

Titanium dioxide (TiO_2) is generally used as one of the most popular photocatalysts in photocatalytic oxidation for water and wastewater treatment, because of its lack of toxicity, chemical inertness, and low cost (24). GT01 has a comparatively good performance in MW/ TiO_2 degradation of PCBs and is easily separated from the contents of the reactor. The concentration of 4g/l has been the optimum dosage of GT01 under experimental condition in terms of catalytic oxidation rate. Microwave enhances the reactants mobility and diffusion leads to the improved exchange of reactants between catalyst surface and solution (24).

As expected, degradation rate of PCBs enhanced with increases in the concentration of added H_2O_2 . This can be explained by the production of additional OH^* radicals (25).

The results of the present study showed that irradiation alone cannot be used as an effective procedure for the degradation of PCBs. Some studies have indicated that degradation efficiency of PCBs by MW radiation could be raised by adding H_2O_2 . When H_2O_2 is added, the dominant mechanism of PCBs destruction becomes hydroxyl radical-mediated advanced oxidation. When highly reactive OH radical species produced in the process are expected to quickly react with PCBs. Hydroxyl radical is an extremely reactive and nonselective oxidant; thus, when produced in sufficient quantities, it can lead to complete oxidation of organic compounds to carbon dioxide, water, and inorganic ions (22). The OH^* radical may oxidize substrate, but because of its high reactivity, it may also react with a variety of other substances commonly found in

PCBs. Hydrogen peroxide dose is a very important parameter for efficiency of the treatment process and its economic desirability. In the MW/ H_2O_2 process, degradation of hydrogen peroxide is the major mechanism that generates hydroxyl radicals. Therefore, it is logical to assume that increase in hydrogen peroxide dose would amplify transient-state concentration of hydrogen peroxide. This is not the case though, because hydrogen peroxide acts as a hydroxyl radical scavenger, too (13, 21-23, 25). It is obvious that at low initial hydrogen peroxide concentrations, increase in its dose significantly amplifies the degradation rate of PCBs.

At higher concentrations, the effect of increasing the dose is negligible. This is a reasonable result since hydroxyl radical production takes away from degradation rate, and further increase in hydrogen peroxide dose from that point acts only to increase hydroxyl radical scavenging from hydrogen peroxide. This reveals that the degradation of PCBs by $\text{H}_2\text{O}_2/\text{TiO}_2$ participated microwave-hydrothermal reaction proceeded very quickly. The total amount of the PCB congeners in the reactor reduced to less than 4% in 9 minutes of microwave irradiation. As Table 2 shows, degradation rate is very high during the first three to four minutes. Then it slows down and levels off when the irradiation proceeds. This indicates that the reactor is highly efficient in dechlorinating of the congeners tested. Optimizing the time for degradation reduces the reaction time and the main cost of the treatment, i.e. energy expenditure of MW radiation can be minimized (2,4,10,20).

An important variable influencing dechlorination is microwave power. Microwave power is regarded as a very important factor for dechlorination reaction because the temperature that the whole reaction system or catalyst can reach is directly related to the power level. Accordingly, a rise in MW power will provide more thermal energy and increase

degradation efficiency (26). NaOH, H₂O₂, TiO₂, and C₂H₅OH receive microwave irradiation at first by space charge polarization and dipolar polarization, and then the incident microwave energy is directly converted into thermal energy (17). Microwave energy has been used more and more on synthetic organic chemistry due to its great ability to accelerate reactions and improve yields and selectivity (27). Recently, some researchers have started to investigate catalytic reactions assisted with microwave irradiation (28,29).

Table 2 shows the effects of changing MW power on the degradation efficiency of PCB congener. Degradation efficiency generally increases with an increase in MW power. Decline in microwave power reduces dechlorination rate. Also, degradation efficiency tends to reach a plateau in 540 w to 900 w (2,4,10,20).

In general, the effect of MW power is expected to be straightforward. Since the major mechanism for generation of hydroxyl radical is degradation of hydrogen peroxide, increase in the power of MW should increase the generation rate of hydroxyl radical and thus oxidation of PCBs (2,21).

CONCLUSION

The optimum conditions for decomposition efficiency of PCBs included a 50ml volume of ratio to solvent with transformer oil (3:1), sodium hydroxide solution (0.2N) 1 cc, use of 20% hydrogen peroxide of total volume of samples, dioxide titanium (0.2g), and irradiation time (9 minutes). Under optimum conditions, decomposition efficiency of PCBs increased.

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