

Decomposition of Askarel Oil by Microwave Radiation and H₂O₂/TiO₂ Agents in Order to Reduce Occupational Hazards

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ABSTRACT

Background: Poly chlorinated biphenyls (PCBs) are the groups of organic chemical material and toxic, persistent, bio accumulate and pose a risk of causing adverse effects to human health and the environment. PCB compounds are caused the different health effects in human depending of age, sex, route of entry, intensity and frequency exposure. This study was conducted to determine the effect of microwave rays, hydrogen peroxide, TiO₂ catalyst and ethanol on the Decomposition of PCBs.

Methods: In this experiment used a MW oven, Pyrex vessel reactor (250ml volume), Pyrex tube connector and condensing system. A 900w domestic MW oven with a fixed frequency of 2450 MHZ was used to provide MW irradiation. Ray powers used in 540, 720 and 900w. The PCB_s were analyzed by GC-ECD

Results: The degradation of total PCB_s in terms of 540, 720 and 900W was 85.03%, 90.32% and 96.87% respectively. The degradation of total PCB_s in terms of ratio to solvent with transformer oil in 1:1, 2:1 and 3:1 was 53.97%, 78.98% and 95.13% respectively. The degradation of total PCB_s in terms of not using of H₂O₂/TiO₂ and using 20% of H₂O₂ and 0.05, 0.1, 0.15 and 0.2 g TiO₂ was 68.78%, 93.97%, 95.13%, 96.18% and 96.87 % respectively.

Conclusion: The Microwave thermal reaction was applied for the dechlorination of PCBs and high efficiencies were obtained. Microwave power and amounts of reactants added are important factors influencing dechlorination efficiency.

Keywords: Askarel, Degradation, H₂O₂, PCB_s.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) belong to persistent organic pollutants (POPs). They had been noticed because of their global distribution, persistence, and toxicity. Removal of these compounds from the environment remains a very different challenge; because the compounds are highly hydrophobic and have very low solubility in water (1). Although production of PCBs has been banned all over the world, they still are

used in a variety of applications when state of affairs permit(2). they were used in a wide range of industrial applications owing to their excellent physical and chemical properties include oil in transformers, hydraulic fluids in hydraulic tools, dielectrics in capacitors, and equipment and heat exchange liquids. Consequently they are bio accumulated and pose great risk to environment and human health. PCB compounds generate different health effects in human dependent on sex, age, intensity and frequency exposure and route

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of entry (3). Incineration is a reliable method for destruction of PCBs in transformer oil. It can destroy over 99.9999% of PCBs and is widely used (3, 4); however there is widespread public resistance to this approach down to potential for lease of dioxin via flue, when they stream (5). Now it is compulsory to accept non-combustion technologies for handling of PCBs containing wastes. Alternative treatments 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 (6-13). In recent years microwave irradiation has been applied for decomposition or dechlorination of chlorinated organic pollutants. In this field a series of pioneer studies had been carried out; as shown by Abramovitch et al (1998-1999) who adopted microwave irradiation for remediation of PCBs polluted soil and the results were attractive (14,15). Subsequently Raquel et al (2002) investigated microwave decomposition of lindane supported on modified sepiolites, and found that trichlorobenzene and pentachlorocyclohexene formed with NaOH-modified sepiolite in a short time microwave irradiation (16). Most of the dechlorinating processes for wastes containing PCBs were carried out in various organic solvents (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).

MATERIAL AND METHODS

This was an experimental study carried out in the laboratory of Tarbiat Modares University.

Chemicals

Oil transformers were obtained from regional Electric Company in Tehran. Ethanol (C₂H₅OH), sodium hydroxide (NaOH) (all p. apquality, Merck) and hydrogen peroxide (H₂O₂, Merck) are used without any purification prior to use. Grain

TiO₂ was GT01 (HSD co, China), the particle diameter of GT01 was 180-250 μm which is small enough for suspension; but large enough for settlement by gravity. The BET surface area of GT01 is 194.4 m²/g and density is 900kg/m³.

Equipments

In the MW oven (380mm×380mm×300mm,900w maximal MW output, made in LG company), there was a flat bottom flask(250ml), with which a 600mm long water reflux condenser was connected through a communication pipe. An aperture was made at the top of the oven to the communication pipe can get through. Note that an aluminum tube fixed in the aperture was used to eliminate MW leaking. The limit on the safe stray leakage of MW power density was kept below 0.5 mw/cm² at 2450 MHZ measured at 200mm distance from the aperture. Ray powers used in 540,720 and 900w. Temperature in the flask was measured by quickly stopping the MW oven and was found to be less than 80°C.

Experimental procedures

Transformer oil was dissolved in ethanol of hydroxyl group. Volumes of ethanol and transformer oil were 1:1, 2:1, and 3:1 in various samples. Rapid raise in temperature of the contents of the reactor as a result of microwave radiation was aimed to control the reactor during the reaction conditions; whilst radiation was discontinuous. Thus after several trials radiation was continued for 10 seconds with intervals of 30, 40, and 50 seconds between stages of radiation for the selected exposure times of 3, 6, and 9 minutes respectively. The reaction mixture inside the reactor was continuously stirred the samples contained appropriate volume of oil contaminated by PCBs, ethanol, sodium hydroxide solution (0.2 N), hydrogen peroxide (10% and 20%), and dioxide titanium (0.05, 0.1,0.15 and 0.2g). Adjustment of pH of the solution was done for each assay using NaOH solution. H₂O₂ concentrations and TiO₂ quantities used

were 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 microwave for the same exposures. PCB and solvent molecules were vibrated to maintain uniformity of solution during microwave irradiation and electric field radiation. Some samples were used as control to determine effectiveness of the solution parameters through degradation of oil. The controls were treated similarly but were not irradiated to verify probable losses unrelated to the reaction.

Analysis

The PCBs were analyzed by GC/ECD method (Trace GC ultra USA) with decachlorobiphenyl as internal standard. Data were analyzed by spss software version 16.0 using repeated measurement ANOVA and t-test. P values less than 0.05 were considered significant. Analysis of resulting byproducts was performed at the laboratory of Kimia

shengerf Pars company of Iran by GC/MS. The samples were taken at different time intervals (3, 6, and 9 minutes) and were analyzed immediately or stored at 4°C until 3-5h before analysis. The samples were covered with aluminum foils to protect from exposure of UV radiation.

RESULTS

Identified PCBs in PCB transformer oil included PCB149, PCB170, and PCB194. Initial concentrations of PCBs in addition to percents of degradation of PCBs without solvent, H₂O₂ and TiO₂ are demonstrated in table 1.

Table 2 shows effects of power of microwave in comparable times in samples. The degradation of total PCBs in terms of 540, 720, and 900w was 85.03%, 90.32%, and 96.87% respectively.

Table 3 and figure 1 shows effects of volume of solvent, i.e. ethanol on PCBs degradation. The degradation of total PCBs in terms of ratio of solvent to oil transformer in 1:1, 2:1 and 3:1 was 53.97%, 78.98% and 95.13%.

Table 1. initial concentration of PCBs in PCB transformer oil*

PCB	PCB149	PCB170	PCB194
concentration (µg/L)	1358	1022	667
% of degradation of PCBs (blank sample-without ethanol, H ₂ O ₂ and TiO ₂)	4.49	2.54	2.39

*:Experimental conditions: PH= 7±0.5, Temperature=76±1.5°C, exposure time= 9 min, power=900w

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

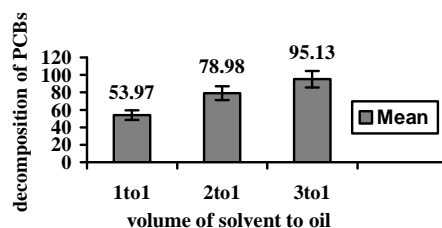
Power	PCBs Exposure Time (min)	PCB149	PCB170	PCB194	Mean
540w	3	82.03	83.17	83.20	82.8
	6	83.50	83.95	84.40	83.95
	9	84.97	85.12	85.007	85.03
720w	3	87.33	87.86	87.40	87.53
	6	88.21	88.25	89.20	88.55
	9	89.98	90.60	90.40	90.32
900w	3	94.99	93.73	94.60	94.44
	6	95.87	94.91	95.80	95.52
	9	96.75	96.86	97.001	96.87

*: Experimental conditions: Volumes 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 (%)*

Volume of solvent to oil	PCBs			Mean
	PCB 149	PCB 170	PCB 194	
1:1	54.19	53.62	54.12	53.97
2:1	78.79	78.86	79.31	78.98
3:1	95.28	94.91	95.20	95.13

*: Experimental conditions: PH= 7 ± 0.5 , Temperature= $74 \pm 1.5^\circ\text{C}$, exposure time= 9 min, power=900w

Figure1. 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= $74 \pm 1.5^\circ\text{C}$, exposure time= 9 min, power=900w

Table 4 shows effects of degradation of PCBs in terms of not using of $\text{H}_2\text{O}_2/\text{TiO}_2$ or using 10% or 20% H_2O_2 with 0.05, 0.1, 0.15, and 0.2 g TiO_2 . Degradation of total PCBs in terms of not using of $\text{H}_2\text{O}_2/\text{TiO}_2$, using 10% H_2O_2 and 0.05, 0.1, 0.15, and 0.2 g TiO_2 were 68.78%, 89.77%, 91.21%, 92.04%, and 93.22% respectively. Degradation of total PCBs in terms of not using of H_2O_2 and 0.05, 0.1, 0.15, and 0.2 g TiO_2 were 68.78%, 93.97%, 95.13%, 96.18%, and 96.87%.

Table 4. Effect of Hydrogen Peroxide and dioxide titanium on PCBs degradation (%)*

$\text{H}_2\text{O}_2/\text{TiO}_2$	PCBs			Mean
	PCB149	PCB170	PCB194	
Not using $\text{H}_2\text{O}_2/\text{TiO}_2$	67.30	70.25	68.81	68.78
10% H_2O_2 + 0.05 g TiO_2	89.69	89.82	89.80	89.77
10% H_2O_2 + 0.1 g TiO_2	90.86	91.78	91.004	91.21
10% H_2O_2 + 0.15 g TiO_2	91.75	92.17	92.20	92.04
10% H_2O_2 + 0.2 g TiO_2	92.93	93.34	93.40	93.22
20% H_2O_2 + 0.05 g TiO_2	93.81	94.12	94.002	93.97
20% H_2O_2 + 0.1 g TiO_2	95.28	94.91	95.20	95.13
20% H_2O_2 + 0.15 g TiO_2	96.46	95.69	96.40	96.18
20% H_2O_2 + 0.2 g TiO_2	96.75	96.86	97.001	96.87

*: Experimental conditions: volume of ethanol and transformer oil (3:1), pH= 7 ± 0.5 , Temperature= $74 \pm 1.5^\circ\text{C}$, exposure time= 9 min, power=900w

DISCUSSION

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 indicated that the reactor is highly efficient in dechlorination of the congeners tested. Optimizing the time for degradation reduces the reaction time and main cost of the treatment, i.e. energy expenditure of MW radiation can be minimized (7-9, 17).

An important variable influence on dechlorination is Microwave power. Microwave power is regarded as a very important factor for dechlorination reaction; because the temperature that whole reaction system or catalyst can reach is directly related to the power level. As a result raise in MW power will provide more thermal energy and increase degradation efficiency (19). 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 (20). Microwave energy has been used more and more on synthetic organic chemistry because of its great ability to accelerate reactions and to improve yields and selectivity (21). Recently, some researchers have started to investigate catalytic reactions assisted with microwave irradiation (22-23).

Table2 shows effects of changing MW power on the degradation efficiency of PCB congener. Degradation efficiency generally increases with raise in MW power. Decline in microwave power reduces dechlorination rate. Also degradation efficiency tends to reach plateau in 540 w to 900 w (7-9, 17).

In general, effect of MW power is expected to be straightforward. Since major mechanism for generation of hydroxyl radical is degradation of hydrogen peroxide, increase in power of MW should raise generation rate of

hydroxyl radical and thus oxidation of PCBs (17, 24).

As the microwave oven used in present study was a modified one, the power levels used here were discontinuous, just timed mark/space ratio can be controlled. Three power levels (540w, 720w, and 900w) were investigated. Other parameters were as follow: 10% and 20% concentration of H₂O₂ (0.058 mol and 0.116 mol), 0.05, 0.1, 0.15 and 0.2g TiO₂, NaOH 0.2 N (1cc), 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 (37.5cc ethanol and 12.5cc oil), and 3, 6 and 9 min Microwave irradiation time.

Six reactants participated in both Microwave thermal reaction and dechlorination process. So the amounts of the reactants being added are crucial and their effects were investigated by adding 0.116 mol of H₂O₂, 0.2g TiO₂, 900w power, NaOH 1 cc, 9min exposure time and 3:1 ratio to solvent; while high oil efficiency of dechlorination was obtained. Therefore, we designed experiments to investigate effects of reduced amounts of reactants on dechlorination. Dechlorination efficiency was calculated based on chlorine ions produced.

Because all chlorobiphenyls are poorly soluble in water, early works on PCB degradation were carried out in alkanes and alcohols. Many organic solvents had been employed in previous studies. Solvents such as hexane, isooctane, 2-propanol and methanol had been used by some researchers (7, 9, and 17). Overall photochemistry in both organic and aqueous media is predominantly dechlorination, nevertheless depending on the solvent used, some solvent derivatives can also be found (8,13,24-26).

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 were few reports found

that have employed ethanol for the purpose. It is reasonable to predict that performance of ethanol should be similar to other solvents. Some solvents, for example hexane and isooctane are highly flammable. When degradation takes long time for high PCB concentration, fire hazard will be of concern. However, reaction rate of PCB was found to be faster in hydroxylic solvents than non-polar solvents (24). We used ethanol solution as intermediate solvent to absorb thermal energy of microwave irradiation and spread it.

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

As expected, degradation rate of PCBs enhanced with increase in concentration of added H_2O_2 . This can be explained by production of additional OH^\cdot radicals (27).

Results of 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 the addition of H_2O_2 . When H_2O_2 is added, the dominant mechanism of PCBs destruction becomes hydroxyl radical mediated advanced oxidation. Highly reactive OH^\cdot radical species produced in the process are expected to quickly react with PCBs. Hydroxyl radical is extremely reactive and nonselective oxidant; thus, when produced in sufficient quantities, can lead to complete oxidation of organic compounds to carbon dioxide, water, and inorganic ions (25).

The OH^\cdot radical may oxidize substrate, but because of its high reactivity it also may react with a variety of other substances commonly found in PCBs.

Hydrogen peroxide dose is 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 dose of hydrogen peroxide 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, 24-27).

It is obvious that at low initial hydrogen peroxide concentrations, increase in its dose significantly amplify degradation rate of PCBs. At higher concentration, effect of increasing the dose is negligible. This is a reasonable result; since hydroxyl radical production take away from degradation rate, than further increase in hydrogen peroxide dose from that point acts only to rise hydroxyl radical scavenging from hydrogen peroxide.

Titanium dioxide (TiO_2) is generally used as one of the most popular photo catalysts in photo catalytic oxidation for water and wastewater treatment, because of its no toxicity, chemical inertness and low costs (28). GT01 has a comparatively good performance in MW/ TiO_2 degradation of PCBs and is easily separated from the contents of 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 improved exchange of reactants between catalyst surface and solution (28).

CONCLUSION

Microwave thermal reaction can be applied for the dechlorination of PCBs with high efficiency. Microwave power and amounts of reactants added are important factors influence on dechlorination efficiency.

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