



THE EFFECT OF SOLVENT, HYDROGEN PEROXIDE AND DIOXIDE TITANIUM ON DEGRADATION OF PCBs, USING MICROWAVE RADIATION IN ORDER TO REDUCE OCCUPATIONAL EXPOSURE

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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. A 900 W domestic microwave oven, pyrex vessel reactor, pyrex tube connector and condensing system were used in this experiment. Radiation was discontinuous and ray powers were 540, 720 and 900 W. The PCB_s were analyzed by GC-ECD. The application of microwave radiation and H₂O₂/TiO₂ agents for the degradation of polychlorinated biphenyl contaminated oil was explored in this study. PCB – contaminated oil was treated in a pyrex reactor by microwave irradiation at 2450 MHz with the addition of H₂O₂/TiO₂. A novel grain TiO₂ (GT01) was used. The determination of PCB residues in oil by gas chromatography (GC) revealed that rates of PCB decomposition were highly dependent on microwave power, exposure time, ratio to solvent with transformer oil in 3:1, the optimal amount of GT01 (0.2 g) and 0.116 mol of H₂O₂ were used in the study. It was suggested that microwave irradiation with the assistance of H₂O₂/TiO₂ might be a potential technology for the degradation of PCB – contaminated oil. The experiments show that MW irradiation, H₂O₂ oxidant and TiO₂ catalyst lead to a degradation efficiency of PCBs only in the presence of ethanol. The results showed that the addition of ethanol significantly enhanced degradation efficiency of PCBs.

INTRODUCTION

There is increasing global concern regarding the utilization and discharge of polychlorinated biphenyl (PCB) compounds into the environment. The removal

of these compounds from the environment remains a very difficult challenge because the compounds are highly hydrophobic and have a very low solubility in water [1]. Polychlorinated biphenyls (PCBs) have been produced since the 1930s, with particularly large volume to the 1970s [2]. For several decades, PCBs have been used in a wide range of industrial applications because of their excellent physical and chemical properties, such as: oil in transformers, dielectrics in capacitors, hydraulic fluids in hydraulic tools and equipment and heat exchange liquids [3, 4]. PCBs also found widespread use as lubricants for turbines and pumps, in the formulation of cutting oils for metal treatment, and to a lesser extent, in applications such as adhesives, carbonless copy paper, dyes, pesticides, surface coatings, plasticizers and waxes [2–13]. Polychlorinated biphenyls are toxic, persistent, bio-accumulative and pose a risk of causing adverse effects to human health and the environment. For various social, technical and economic reasons, significant quantities of PCBs contaminated transformer oil are still in use or in storage [4, 7, 8, 13, 14]. Most of the dechlorinating processes for wastes containing PCBs were carried out in various organic solvents [2–4, 6–9, 15]. 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 [2–4, 6–9, 15].

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 [3–7, 15]. 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, 4, 6–9, 15, 16]. In recent years, microwave irradiation has been applied for the decomposition or dechlorination of chlorinated organic pollutants. In this field, a series of pioneer studies were carried out by Abramovitch et al., who adopted microwave irradiation for the remediation of PCBs polluted soil and the results were attractive [17, 18]. Subsequently Raquel et al., investigated microwave decomposition of lindane supported on modified sepiolites, and found that trichlorobenzene and pentachlorocyclohexene formed with NaOH-modified sepiolite in a short time of microwave irradiation [19]. Most of the dechlorinating processes for wastes containing PCBs were carried out in various organic solvents [2–4, 6–9, 15]. We believe that microwave heating can be employed as energy input to replace conventional heating to accelerate the thermal reaction [20]. This study was conducted to determine the effect of MW radiation, hydrogen peroxide, dioxide titanium and solvent on the degradation of PCBs including PCB in transformer oil.

EXPERIMENTAL

Materials

Ethanol (C_2H_5OH), sodium hydroxide (NaOH) (all p.a. quality, Merck) and hydrogen peroxide (H_2O_2 , Merck) were used without further purification. The Grain TiO_2 was GT01 (HSD Co China). The particle diameter of GT01 was 180–250 μm , which was small enough for suspension but large enough for settlement by gravity. The BET surface area of GT01 was 194.4 m^2/g and density was 900 kg/m^3 . Oil transformers were obtained from Regional Electric Company in Tehran.

Equipments

In the MW oven (380 mm \times 380 mm \times 300 mm, 900 W maximal MW output, made in LG Company), there was a flat bottom flask (250 ml), with which a 600 mm long water reflux condenser was connected through a communication pipe. An aperture was made at the top of the oven for the communication pipe to 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/cm^2 at 2450 MHz measured at 200mm distance from the aperture.

Ray powers were 540, 720 and 900 W. Temperature in the flask was measured by quickly stopping the MW oven and was found to be less than 78°C.

Experimental condition

The four reactants of hydrothermal reaction, ethanol solvent, sodium hydroxide, dioxide titanium and peroxide hydrogen together with transformer oil were put into the pyrex reactor and heated by microwave irradiation. The top of the reactor outside the microwave oven was connected to a condensing system. As the microwave oven used in this study was a modified one, the power levels used here were discontinuous, just timed mark/space ratio control. Three power levels (540 W, 720 W and 900 W) were investigated, and other parameters were as follows: 10% and 20% of H_2O_2 (0.058 mol and 0.116 mol), 0.05, 0.1, 0.15 and 0.2 g TiO_2 , NaOH 0.2 N (1 ml), ratio ethanol solvent with transformer oil 1:1 (25 ml ethanol and 25 ml oil), 2:1 (33.33 ml ethanol and 16.67 ml oil) and 3:1 (37.5 ml ethanol and 12.5 ml oil) and 3, 6 and 9 min microwave irradiation.

The six reactants participated in both the microwave thermal reaction and the dechlorination process. So the amounts of reactants being added are crucial and their effects should be investigated by adding 0.116 mol of H_2O_2 , 0.2g of TiO_2 , 900 W power, 1 ml of NaOH. Both 9 min exposure time and 3:1 ratio to solvent with oil high efficiency of dechlorination was obtained. Therefore, we designed experiments to investigate the effect of reduced amounts of reactants on dechlorination and dechlorination efficiencies were calculated based on chlorine ions produced. The reason why energy equal 900 W was selected for further research is that out of three powers (540 W, 720 W and 900 W) energy equal 900 W showed higher efficiency in degradation of PCBs than the rest of powers and also in the article it is recommended that researchers use from 900 W power in further research.

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 get the organic phase and the aqueous phase. Transformer oil was dissolved in ethanol to dilute and increase its aqueous solubility and donor of hydroxyl group. Rapid raise in temperature of the contents of the reactor as a result of microwave radiation was aimed to control the reactor during the reactor 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 the 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 0.2 g) for each assay the adjustment of the pH of the solution was done using NaOH solution. For the effect of initial PCB concentrations, H_2O_2 concentrations and TiO_2 quantities used were based on the optimum amount obtained, maintaining the PCB/hydrogen peroxide and dioxide titanium ratio in the solution in all the experimental runs. H_2O_2 was used in concentration of 10 and 20% and also TiO_2 was added in the amount of 0.05, 0.1, 0.15 and 0.2 g, because previous researchers selected these amounts and percentages as optimized amounts and percentages. We finally used them, however we tested different amounts and percentages in laboratory. The amounts and percentages selected in the paper confirmed previous research and we used them in our article [21, 22, 23].

For the same exposure, the reactor was on the turn section of microwave. For the uniform of solution as the result of the microwave irradiation under the influence of electric field radiation, PCB and solvent molecules vibrated. In order to determine the effectiveness of the solution parameters on the degradation of oil, samples were used to control. The controls were treated similarly, but not irradiated, in order to determine the losses not due to the reaction.

Chemical analysis

The organic phase was diluted with hexane and decachlorobiphenyl was added as internal standard. The PCBs were analyzed by GC/ECD (Trace Gc Ultra USA). Sample preparation and technical analyses were based on EPA method number 8082. The data were analyzed using statistical software, SPSS16.0 for statistical analyses, repeated measurement ANOVA, t test and $p < 0.05$ were significant. The identification of the resulting products was performed at the laboratory services of Kimia Shengerf Pars Company of Iran by GC/MAS. 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 min) intervals and analyzed immediately or stored at 4°C up to 3–5 h before analysis.

For quality control, the experiments were performed in triplicate and the results are presented as mean values. To prevent exposure to UV irradiation, the samples were covered with aluminium foil. The samples without the H_2O_2/TiO_2 and solvent were also used to investigate the effect of direct degradation of PCBs. The capillary column used was a DB-5 and the carrier gas was helium. The capillary column (narrow-bore) 30 m × 0.32 mm ID fused silica capillary column chemically bonded with 5 percent phenyl methyl and 0.25 μm film thickness. Helium was used as carrier gas with a flow rate of 1.3 mlmin⁻¹ and N_2 was used as make-up gas with a flow rate of 60 mlmin⁻¹. The injector and detector temperatures were set at 280 and 300°C respectively. A split-splitless injector in the

splitless mode was used. The column temperature was programmed as follows: 50°C (30 seconds), 12°Cmin⁻¹ to 130°C and 5°Cmin⁻¹ to 280°C and 5 min hold.

RESULTS AND DISCUSSION

Identified PCBs in PCB transformer oil included PCB105, PCB149, PCB153 and PCB180. The reason for choosing for the research four PCB out of 209 congeners was machine memory limitation, which means that the machine could not give us all of PCBs.

Initial concentrations of PCBs in addition to percentage of degradation of PCBs without solvent, H₂O₂ and TiO₂ are demonstrated in Table 1.

Table 2 and Figure 1 show the effects of power of microwave in comparable times in samples. Degradation of total PCBs in terms of 540, 720 and 900 W was 85.7%, 90.4% and 97%, respectively.

Table 3 and Figure 2 show the effects of volume of solvent, i.e ethanol on PCBs degradation. Degradation of total PCBs in terms of ratio solvent to oil transformer in 1:1, 2:1 and 3:1 was 54.5%, 79.4% and 95.4%.

Table 1. Initial concentration of PCBs in PCB transformer oil

PCB	PCB105	PCB149	PCB153	PCB180
Value (µg/L)	946	1358	1997	3333
degradation (%) of PCBs (blank sample-without ethanol and H ₂ O ₂ and TiO ₂)	0.7	<u>1.49</u>	0.4	2.2

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

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

PCBs Power	Exposure Time (min)	PCB105	PCB149	PCB153	PCB180	Mean
<u>540 W</u>	3	<u>83.5</u>	<u>82.6</u>	<u>84.7</u>	<u>82.9</u>	<u>83.4</u>
	6	<u>84.9</u>	<u>84</u>	<u>85.1</u>	<u>83.9</u>	<u>84.5</u>
	9	<u>86</u>	<u>85.5</u>	<u>86.2</u>	<u>85.1</u>	<u>85.7</u>
<u>720 W</u>	3	<u>88.8</u>	<u>88</u>	<u>88.1</u>	<u>86.8</u>	<u>87.9</u>
	6	<u>90</u>	<u>89</u>	<u>88.7</u>	<u>87.7</u>	<u>88.9</u>
	9	<u>91</u>	<u>90.2</u>	<u>90</u>	<u>90.5</u>	<u>90.4</u>
<u>900 W</u>	3	<u>93.9</u>	<u>95</u>	<u>93.8</u>	<u>93.8</u>	<u>94.1</u>
	6	<u>95.1</u>	<u>96</u>	<u>94.8</u>	<u>95.9</u>	<u>95.5</u>
	9	<u>96.2</u>	<u>97.1</u>	<u>97.3</u>	<u>97.4</u>	<u>97</u>

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

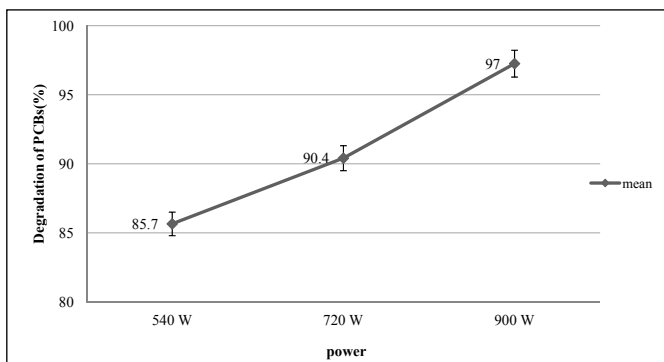


Fig. 1. Effect of microwave intensity on PCBs degradation(%)

Experimental conditions: Volumes of ethanol and transformer oil (3:1), pH = 7 ± 0.5 , Temperature in 540 W = $37\pm 1.5^\circ\text{C}$ (3 min), $41\pm 1.5^\circ\text{C}$ (6 min) and $46\pm 1.5^\circ\text{C}$ (9 min), In 720 W = $51\pm 1.5^\circ\text{C}$ (3 min), $55\pm 1.5^\circ\text{C}$ (6 min) and $60\pm 1.5^\circ\text{C}$ (9 min), In 900 W = $65\pm 1.5^\circ\text{C}$ (3 min), $69\pm 1.5^\circ\text{C}$ (6 min) and $74\pm 1.5^\circ\text{C}$ (9 min)

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

Volume of solvent to oil	PCBs				
	PCB105	PCB149	PCB153	PCB180	Mean
1:1	<u>53.8</u>	<u>54.7</u>	<u>54.9</u>	<u>54.7</u>	<u>54.5</u>
2:1	<u>79.1</u>	<u>79.2</u>	<u>79.9</u>	<u>79.5</u>	<u>79.4</u>
3:1	<u>95.1</u>	<u>95.9</u>	<u>95.6</u>	<u>95.1</u>	<u>95.4</u>

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

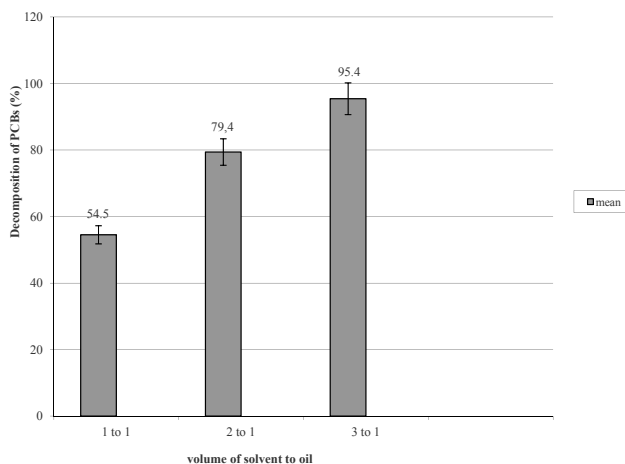


Fig. 2. Effect of volume of solvent on PCBs degradation

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 = 900 W

Table 4 and Figure 3 show the effects of initial H_2O_2 concentration on the degradation of PCBs with use of MW/ H_2O_2 process. Degradation of PCBs in terms of use of 10% and 20% of total volume in samples of H_2O_2 was 85% and 89.3%, respectively.

Table 5 and Figure 4 show the effects of degradation of PCBs in terms of not using H_2O_2/TiO_2 and using 10% and 20% of H_2O_2 and 0.05, 0.1, 0.15 and 0.2 g TiO_2 . Degradation of total PCBs in terms of not using H_2O_2/TiO_2 and using 10% of H_2O_2 and 0.05, 0.1, 0.15 and 0.2 g TiO_2 was 70.3%, 89%, 90.4, 92.2% and 93.2%, respectively. Degradation of total PCBs in terms of not using H_2O_2/TiO_2 and using 20% of H_2O_2 and 0.05, 0.1, 0.15 and 0.2 g TiO_2 was 70.3%, 93.9%, 95.1%, 96.2 % and 97.1%.

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

PCBs Peroxide Hydrogen	Time (min)	PCB105	PCB149	PCB153	PCB180	Mean
10% H_2O_2	3	<u>82.2</u>	<u>83</u>	<u>82.9</u>	<u>83.8</u>	<u>83</u>
	6	<u>83.9</u>	<u>84.4</u>	<u>84.7</u>	<u>84.2</u>	<u>84.3</u>
	9	<u>85.1</u>	<u>85</u>	<u>85</u>	<u>84.8</u>	<u>85</u>
20% H_2O_2	3	<u>88.3</u>	<u>86.4</u>	<u>86.5</u>	<u>86.2</u>	<u>86.9</u>
	6	<u>89.4</u>	<u>87.2</u>	<u>87.9</u>	<u>87.1</u>	<u>87.9</u>
	9	<u>90.5</u>	<u>88.5</u>	<u>89.8</u>	<u>88.2</u>	<u>89.3</u>

Experimental conditions: Volumes of ethanol and transformer oil (3:1), pH = 7 ± 0.5 , Temperature = $65 \pm 1.5^\circ C$ (3 min), $69 \pm 1.5^\circ C$ (6 min) and $74 \pm 1.5^\circ C$ (9 min), power = 900 W

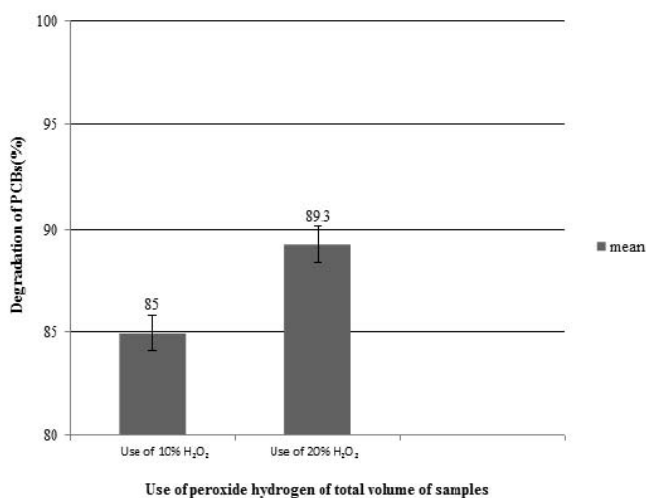


Fig. 3. Effect of hydrogen peroxide on PCBs degradation (%)

Experimental conditions: volume of ethanol and transformer oil (1:1, 2:1 and 3:1), pH = 7 ± 0.5 , Temperature = $74 \pm 1.5^\circ C$, exposure time = 9 min, power = 900 W

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

H ₂ O ₂ /TiO ₂ \ PCBs	PCB105	PCB149	PCB153	PCB180	Mean
Not using of H ₂ O ₂ /TiO ₂	<u>69.6</u>	<u>67.3</u>	<u>71.6</u>	<u>72.6</u>	<u>70.3</u>
10% H ₂ O ₂ + 0.05 g TiO ₂	<u>88.5</u>	<u>89.9</u>	<u>89</u>	<u>88.6</u>	<u>89</u>
10% H ₂ O ₂ + 0.1 g TiO ₂	<u>89.8</u>	<u>91</u>	<u>90.9</u>	<u>90</u>	<u>90.4</u>
10% H ₂ O ₂ + 0.15 g TiO ₂	<u>92.4</u>	<u>92.1</u>	<u>92.4</u>	<u>91.8</u>	<u>92.2</u>
10% H ₂ O ₂ + 0.2 g TiO ₂	<u>93.2</u>	<u>93.9</u>	<u>93</u>	<u>92.5</u>	<u>93.2</u>
20% H ₂ O ₂ + 0.05 g TiO ₂	<u>93.9</u>	<u>94.8</u>	<u>94</u>	<u>93</u>	<u>93.9</u>
20% H ₂ O ₂ + 0.1 g TiO ₂	<u>95.1</u>	<u>95.9</u>	<u>95.2</u>	<u>94.3</u>	<u>95.1</u>
20% H ₂ O ₂ + 0.15 g TiO ₂	<u>95.9</u>	<u>96.9</u>	<u>96.2</u>	<u>95.7</u>	<u>96.2</u>
20% H ₂ O ₂ + 0.2 g TiO ₂	<u>96.9</u>	<u>97.5</u>	<u>98</u>	<u>95.9</u>	<u>97.1</u>

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

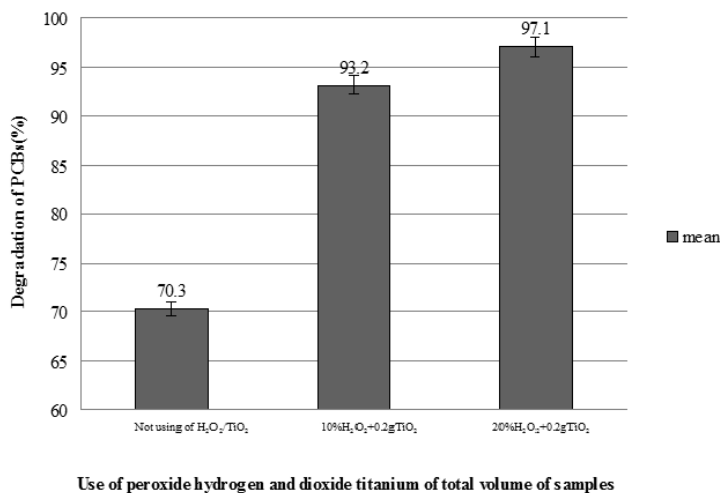


Fig. 4. Effect of hydrogen peroxide on PCBs degradation (%)
 Experimental conditions: volume of ethanol and transformer oil (3:1), pH = 7±0.5
 Temperature = 74±1.5°C, exposure time = 9 min, power = 900 W

Effect of MW power

The result of Table 2 show that the degradation rate was very high during the first three, four minutes, but the degradation decreased when the irradiation was continued. This indicated that the reactor was highly efficient in dechlorinating the congeners tested, and optimizing the time for degradation reduced the reaction time and therefore the main cost of the treatment, i.e. energy cost of producing MW radiation can be minimized [2, 6, 7, 15].

An important variable influencing dechlorination is microwave power. Microwave power was regarded as a very important factor for the dechlorination reaction, because the temperature that the whole reaction system or catalyst could reach was directly related to the power level, as a result, increasing the MW power will provide more thermal energy and so increase the degradation efficiency [24]. At first, NaOH, H₂O₂, TiO₂ and C₂H₅OH received microwave irradiation by space charge polarization and dipolar polarization, and the incident microwave energy was instantly converted into thermal energy [25]. Microwave energy has been used more and more in synthetic organic chemistry because of its great ability to accelerate reactions and to improve yields and selectivity [26]. Recently, some researchers have started to investigate catalytic reactions assisted with microwave irradiation [27, 28].

Figure 1 shows the effect of changing MW intensity on the degradation efficiency of PCB congeners. In general, the degradation efficiency increased with increasing MW intensity and decreasing the microwave intensity decreasing the dechlorination rate, and also the degradation efficiency tended to plateau from 540 W to 900 W [2, 6, 7, 15].

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, increasing the power of MW should increase the generation rate of hydroxyl radical and thus the oxidation of the PCBs [2, 6, 7, 15, 29].

Effect of ethanol(solvent)

Figure 2 shows the effect of changing volume of solvent on the degradation efficiency of PCB congeners. The degradation of total PCBs in terms of ratio to solvent with transformer oil in 1:1, 2:1 and 3:1 was 54.5%, 79.4% and 95.4%, respectively. Because all chlorobiphenyls are poorly soluble in water, early work on PCB degradation was carried out on 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, 6, 7]. 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 [10–12, 15, 29]. Photochemical decomposition using alkaline isopropyl alcohol would not be useful in aqueous media because water inhibits the reaction by protonating the reactive radical. It was reasonable to predict that the performance of ethanol should be comparable or equal to other solvents. Some of solvents, for example, hexane and isooctane are highly flammable, and the degradation may take long time for high PCB concentration, fire hazard is of concern. However, the reaction rate of PCB was found to be faster in hydroxylic solvents than in non-polar solvents [29]. We used ethanol solution as intermediate solvent for absorbing thermal energy of microwave irradiation and spreading it.

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

Effect of hydrogen peroxide

Figure 3 shows the effect of initial H_2O_2 concentration on the degradation of PCBs with use of MW/ H_2O_2 process. The degradation of total PCBs in terms of use of 10% and 20% of volume of H_2O_2 was 85% and 89.3%, respectively. As expected, the degradation rate of PCBs increased with increasing the concentration of H_2O_2 added. This can be explained by the effect of the additionally produced OH^* radicals [13].

Results showed that irradiation alone cannot be used as an effective procedure for the degradation of PCBs. Some studies indicated that the 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, 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 [11]. 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 a very important parameter for the efficiency of the treatment process and the economic desirability. In the MW/ H_2O_2 process, the degradation 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 [10–13]. It is obvious that at low initial hydrogen peroxide concentrations, increasing the dose significantly increases 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 degradation rate, increasing the hydrogen peroxide dose further from that point acts only to increase the hydroxyl radical scavenging from hydrogen peroxide.

Effect of dioxide titanium

Table 5 and Figure 4 show $\text{H}_2\text{O}_2/\text{TiO}_2$ influence on PCB degradation, as the results indicate that microwave radiation in $\text{H}_2\text{O}_2/\text{TiO}_2$ presence best influences PCB degradation (97.1%), whereas for other experiments in 95.4% and 89.3%. Titanium dioxide (TiO_2) powder is generally used as one of the most popular photocatalysts in photocatalytic oxidation for water and wastewater treatment because of its nontoxicity, chemical inertness and low costs [30]. GT01 had a comparatively good performance in MW/ TiO_2 degradation PCBs and was easily separated from the contents of reactor. The concentration of 4 g/l (0.2 g/50 ml) was the optimum dosage of GT01 under the experimental condition in terms of catalytic oxidation rate. Microwave enhances the reactants mobility and diffusion leading to increased exchange of reactants between catalyst surface and solution [30].

CONCLUSION

The microwave-thermal reaction was applied for the dechlorination of PCBs and high efficiencies were obtained. The results have shown that microwave power and amounts of reactants added are important factors influencing dechlorination efficiency. At larger microwave output power, the temperature of reactor rises more rapidly and the degradation process of PCBs in oil is accelerated. Dechlorination can be completed in very short time under microwave irradiation. For the purpose of more completed decomposition, the optimal decomposition efficiency was observed when solution volume of 50 ml, 0.116 mol H₂O₂, 0.2 g TiO₂, 900 W power, NaOH 1 ml, 9-min exposure time and 3:1 ratio to solvent with oil were used in the study. This method is effective in degrading PCBs and it might be applicable in PCB-polluted oil in the future and also might provide an option for the treatment of POPs-containing wastes.

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REFERENCES

- [1] Fang Y. & Al-Abed S.R. (2008). Dechlorination kinetics of monochlorobiphenyls by Fe/Pd: Effects of solvent, temperature, and PCB concentration, *Applied Catalysis B: Environmental*, 78, 3–4, 371–380.
- [2] Wong K.H. & Wong P.K. (2006). Degradation of polychlorinated biphenyls by UV-catalyzed photolysis, *Human and Ecological Risk Assessment*, 12, 2, 259–269.
- [3] Wenhai Wu., Jie Xu, Hongmei Z., Zhang Q. & Liao S. (2005). A practical approach to the degradation of polychlorinated biphenyls in transformer oil, *Chemosphere*, 60, 7, 944–950.
- [4] Borja J., Taleon D.M., Auresenia J. & Gallardo S. (2005). Polychlorinated biphenyls and their biodegradation, *Process Biochemistry*, 40, 6, 1999–2013.
- [5] Shih Y.H. & Wang C.K. (2009). Photolytic degradation of polybromodiphenyl ethers under UV-lamp and solar irradiations, *Journal of Hazardous Materials*, 165, 1–3, 34–38.
- [6] Manzano M.A., Perales J.A., Sales D. & Quiroga J.M. (2004). Using solar and ultraviolet light to degrade PCBs in sand and transformer oils, *Chemosphere*, 57, 7, 645–654.
- [7] Chang F.C., Chiu T.C., Yen J.H. & Wang Y.S. (2003). Dechlorination pathways of ortho-substituted PCBs by UV irradiation in n-hexane and their correlation to the charge distribution on carbon atom, *Chemosphere*, 51, 8, 775–784.
- [8] Leaes F.L., Daniel A.P., Mello G.B., Battisti V., Bogusz Jr. & Emanuelli T. (2006). Degradation of polychlorinated biphenyls (PCBs) by staphylococcus xylosus in liquid media and meat mixture, *Food and Chemical Toxicology*, 44, 6, 847–854.
- [9] Wiegel J. & Wu Q. (2000). Microbial reductive dehalogenation of polychlorinated biphenyls, *FEMS Microbiology Ecology*, 32, 1, 1–15.
- [10] Lin Y.J., Chen Y.L., Huang C.Y. & M.F. Wu (2006). Photocatalysis of 2,2',3,4,4',5-hexachlorobiphenyl and its intermediates using various catalytical preparing methods, *Journal of Hazardous Materials*, 136, 3, 902–910.
- [11] Xue L., Lei F., Jun H. & Gang Y. (2008). Photolysis of mono- through deca-chlorinated biphenyls by ultraviolet irradiation in n-hexane and quantitative structure-property relationship analysis, *Journal of Environmental Sciences*, 20, 6, 753–759.
- [12] Lin Y., Teng L.S., Lee A. & Chen Y.L. (2004). Effect of photosensitizer diethylamine on the photodegradation of polychlorinated biphenyls, *Chemosphere*, 55, 6, 879–884.
- [13] Katsumata H., Kaneco S., Suzuki T., Ohta K., Yobiko Y. (2006). Degradation of polychlorinated dibenzo-p-dioxins in aqueous solution by Fe (II)/H₂O₂/UV system, *Chemosphere*, 63, 4, 592–599.

- [14] Agency for Toxic Substances and Disease Registry. Toxicological profile for polychlorinated biphenyls (PCB). ATSDR, Division of Toxicology/Toxicology Information Branch, 2000.
- [15] Xitao L. & Gang Y. (2006). Combined effect of microwave and activated carbon on the remediation of polychlorinated biphenyl-contaminated soil, *Chemosphere*, 63, 2, 228–235.
- [16] Kastanek F., Maletterova Y., Kastanek P., Rott J., Jiricny V. & Jiratova K. (2007). Complex treatment of wastewater and groundwater. Contaminated by halogenated organic compounds, *Desalination*, 211, 1, 261–271.
- [17] Abramovitch R.A., Huang B.Z., Mark D. & Luke P. (1998). Decomposition of PCBs and other polychlorinated aromatics in soil using microwave energy, *Chemosphere*, 37, 8, 1427–1436.
- [18] Abramovitch R.A., Huang B.Z., Abramovitch D. & Asong J. (1999). Decomposition of PCBs in soil using microwave energy, *Chemosphere*, 38, 10, 2227–2236.
- [19] Salvador R., Casal B., Yates M., Martin-Luengo M. & Ruiz-Hitzky E. (2002). Microwave decomposition of a chlorinated pesticide (Lindane) supported on modified sepiolites, *Applied Clay Science*, 22, 3, 103–113.
- [20] Chuang F.W., Larson R.A. & Wessman M.S. (1995). Zero-valent iron-promoted dechlorination of polychlorinated biphenyls, *Environmental Science & Technology*, 29, 9, 2460–2463.
- [21] Dercova K., Vrana B., Tandlich R. & Subovd E. (1999). Fenton's type Reaction and Chemical Pretreatment of PCBs, *Chemosphere*, 39, 15, 2621–2628.
- [22] Xiwang Z., Yizhong W. & Guoting L. (2005). Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO₂ catalyst, *Journal of Molecular Catalysis*, 237, 199–205.
- [23] Jun H., Cheng S., Shao-Gui Y. & Ya-Zi L. (2006). Photocatalytic degradation of methylene blue in TiO₂ aqueous suspensions using microwave powered electrodeless discharge lamps, *Journal of Hazardous Materials*, B133, 162–166.
- [24] Liu X.T., Quan X., Bo L.L., Chen S. & Zhao Y.Z. (2004). Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, *Carbon*, 42, 2, 415–422.
- [25] Kawahara F.K. & Michalakos P.M. (1997). Base-catalyzed destruction of PCBs – new donors new transfer agents/catalysts, *Industrial & Engineering Chemistry Research*, 36, 5, 1580–1585.
- [26] Cirkva V. & Hajek M. (1999). Microwave Photochemistry. Photo initiated radical addition of tetrahydrofuran to perfluorohexylethylene under Microwave irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, 123, 21–23.
- [27] Kataoka S., Tompkins D.T., Zeltner W.A. & Anderson M.A. (2002). Photocatalytic oxidation in the presence of microwave irradiation : observations with ethylene and water, *Journal of Photochemistry and Photobiology A: Chemistry*, 148, 1–3, 323–330.
- [28] Horiyoshi S., Hidaka H. & Serpone N. (2002). Environmental remediation by an integrated microwave/UV-illumination method. Microwave-assisted degradation of rhodamine-B dye in aqueous TiO₂ dispersions, *Environmental Science & Technology*, 36, 6, 1357–1366.
- [29] Yao Y., Kakimoto K., Ogawa H.I., Kato Y., Kadokami K. & Shinohara R. (2000). Further study on the photochemistry of non-ortho substituted PCBs by UV irradiation in alkaline 2-propanol, *Chemosphere*, 40, 9–11, 951–956.
- [30] Li X., Liu H., Cheng F. & Tong H. (2003). Photocatalytic oxidation using a new catalyst TiO₂ microsphere for water and wastewater treatment, *Environmental Science & Technology*, 37, 17, 3989–3994.