Original Article

Combination of microwave radiation and a nucleophile material in alkaline environment on the destruction of aroclor 1262 in real transformer waste oil

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ABSTRACT

Aims: This research was done to assess the dechlorination and destruction of polychlorinated biphenyls (PCBs) in real-waste transformer oil via microwave (MW) radiation.

Materials and Methods: The influence of MW power, reaction time, polyethylene glycol, zero-valent iron powder, sodium hydroxide (NaOH), and water (H_2O) were investigated on the dechlorination and destruction efficiency of PCBs in real-waste transformer oil under MW radiation.

Results: The findings show that polyethylene glycol and NaOH have great influence on destruction of PCBs. However, iron (Fe) did not have any influence, and H_2O decreased the destruction efficiency of PCBs. Moreover, experimental data showed that with optimum amount of variables [ie, polyethylene glycol (PEG) = 5.4 g, NaOH = 1.13g, Fe = 0.6g, H_2O = 0.8 mL, and MW power of 800 W], more than 99.9% of PCBs were destructed at reaction time of 6 min. Furthermore, destruction of PCBs in the absence of water increased up to 100% after 6 min.

Conclusion: Accordingly, results showed that MW radiation and reactants (PEG and NaOH) were very important factors for the destruction of PCBs from real-waste transformer oil.

Key words: Aroclor, dechlorination, microwave, nucleophile, polyethylene glycol

INTRODUCTION

The polychlorinated biphenyls (PCBs) are man-made chlorinated derivatives of biphenyl bearing 1-10 chlorine atoms.[1] PCBs are commercially valuable for special dielectric and insulating properties. These chemical materials have been, and maintain to be, used initially as dielectric fluids and coolants for electrical equipment and other applications.[2] Therefore, they were produced in large amounts for a long period, from 1929 to 1976. Aroclor is a trade name for various groups of PCBs that were produced in Monsanto company in the United States.[3] They are indelible in the environment and normally end in bioaccumulation, they have perilous effects on human and savage life as well.[4] Stockholm convention in May 2004, compulsorily prohibited

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the use of PCBs containing products by 2025, and also made it mandatory to eliminate all of the PCBs containing wastes by 2028.[5,6] To meet the Stockholm convention 2028 deadline, destruction of PCBs in Iran should be carried out by state-of-the-art incineration facilities and/or other modern technologies that are not available in the country; therefore, the local PCB wastes must be exported to industrialized countries that impose high costs to the country. This study was carried out to resolve this problem.

Commercially applicable and well-known treatment technologies for eliminating PCBs from transformer oils are chemical dechlorination as base catalyzed decomposition (BCD), hydro-thermal oxidization decomposition, sodium reduction, photo-disintegration, incinerations, and so on.[7-10]

These technologies have many advantages and disadvantages that have been investigated and applied in various countries. Among which incinerations are the most current, but there is a widespread public objection to this method due to the potential release of dioxin through exhaust stream. Now, some noncombustion technologies have been well developed or are developing, such as gas phase chemical reduction, base-catalyzed decomposition, sodium reduction, and plasma arc.[8]

In recent years, the destruction of chlorinated organic pollutants has been carried out using microwave (MW) irradiation. In this field, Liu *et al* found that the destruction rates of PCBs in soil increase with the application of MW and activated carbon.[8] Kastanek *et al*. investigated the dechlorination of PCBs in waste oil in the presence of nucleophile reactants and a ionic liquid under MW irradiation; they found that MW decomposed over 99.99% of the PCBs after merely 5 min, whereas with conventional heating around 55%-60% of PCBs were destroyed at 60 min.[11] Subsequently, Liu *et al*. investigated the hydrothermal decomposition of PCBs in waste transformer oil in the presence of water (H_2O), zero-valent iron, and sodium hydroxide (NaOH) by MW radiation. They destructed all PCBs via MW hydrothermal decomposition in 10 min.[8] In all the above investigations and other works in this field, MW had mostly influenced the reactions rate. It is proved that in the reaction between polyethylene glycol (PEG) and polychlorinated biphenyls in alkaline environment, it is PCB which is destroyed.[12] In this reaction, PEG as a nucleophile attacks biphenyl rings and separates chlorine ions from PCBs simultaneously. Also, hydrogen production from iron hydrothermal oxidation at temperatures above 300°C is proved.[13] The hydrogen that is produced can be used for the dechlorination of PCBs.

In this study, the above two reactions (PEG + NaOH and Fe + H_2O + NaOH) were used for destruction of PCBs in waste transformer oil under MW.

MATERIALS AND METHODS

Waste transformer oil, contaminated with PCBs, was obtained from a waste oil storage site in Hormozgan, a province in south of Iran. The waste oil contained 19 kinds of PCBs (aroclor 1262), including five, six, and seven chlorinated PCBs (No's 82, 87, 99, 105, 114, 118, 126, 128, 138, 153, 156, 158, 169, 170, 179, 180, 183, 187, and 189).

The detected concentration of aroclor 1262 prior to the process was 7884 mg/L. All required materials were purchased from Merck with grad analytical. Experiments were performed in a modified domestic MW stove with condensing system (2450 MHz, 900 W, Delonghi Co Germany).

A condensing system was installed above the reactor for collecting distillation [Figure 1]. We opened a hole with 35 mm diameter above the MW stove from which a quartz batch reactor (30 mm i.d.) was inserted. The space between the wall and reactor was filled with a Teflon ring. This reactor was connected to a condenser for preventing liquid evaporation, and so the evolved gas passed through two vessels, which were connected in series and contained *n*-hexane. The materials in the reactor were cooled at 6°C after the process ended, and then they were mixed with *n*-hexane in vessels and PCB was detected. All these experiments were carried out in batch reactor. The main operational variables were tested for decomposition of PCBs from waste transformer oil.

First, experimental design was carried out through central composites design (CCD) method (Design-Expert 7 software). The operational variables were used in the CCD follows the radiation time (360 s), MW power levels (200-1000 W), polyethylene glycol (1.5-7.5 g), zero-valent iron powder (0.3-1.5 g), NaOH (0.3-1.5 g), and H_2O (0.4-2 mL), which were selected based on preceding studies and our initial tests. The samples in the first experimental design were 64. The real waste oil amount which was used in all

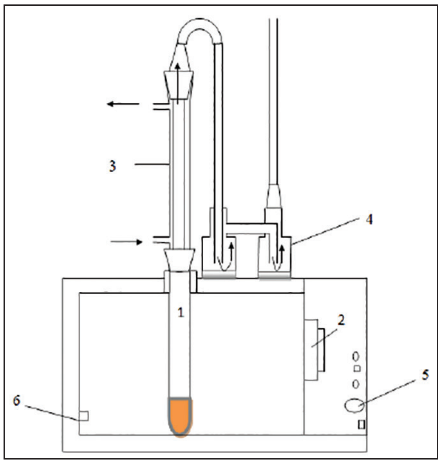

Figure 1: Schematic of experimental set up; 1, Quartz reactor; 2, Microwave lamp; 3, Condenser; 4, Vessels containing hexane; 5, Canterol switch; 6, IR-temperature censor

experiments was 10 mL. Afterwards, the optimum amounts of variables were achieved using the CCD method at 360 s, and then reaction rates were investigated using the optimum amounts of variables ranging from 0 to 600 s. At the end of the experiments, the dechlorination and destruction mechanisms were analyzed. In every stage, duplicate or sometimes triplicate processes were carried out and analyzed. The samples in these runs were 60.

PCBs were analyzed using AGILENT gas chromatography, which was equipped with an electron capture detector (model 6990N), based on standard testing method D 4059, as reported in ASTM. Hexane was used for the dilution of organic phases (1:40). The type of column was DB-5, capillary, diameter 0.32 m, length 30 m, and film thickness 0.25 µm. The injector and detector temperatures were at 270°C and 300°C, respectively. The carrier gas was N_2 with a flow rate of 0.9 mL/min. The column temperature was programmed as follows: Initial temperature was 120°C; first temperatures increase rate was 15°C/min to 210°C in isotherm 1 min; second increase rate was 20°C/min to 240°C in isotherm 2 min; and the third one was 30°C/min to 295°C in isotherm 2 min. The PCBs isotherms were obtained by injecting predetermined concentrations to Gas Chromatography - Electron Capture Detector (GC/ECD).

A VARIAN 4000 Gas chromatography-Mass Spectrometry (GC/MS) was applied for detection of the PCBs degradation byproducts. DB-5 MS and helium were used as capillary column and carrier gas, respectively.

To confirm the possibility of the hydrothermal reaction, acetone and demonized water were used to wash precipitated solid particles; then, they were dried in free environment. Finally, they were portrayed by X-ray diffractometer with Cu Ka radiation.

RESULTS

A very important factor in the dechlorination and destruction of PCBs was MW irradiation; the temperature of the whole process, the radiation intensity of MW, and reaction rate were directly related to the MW power levels.[14,15]

During this research, the MW power levels were 180, 360, 540, 720, and 900 W; other factors were as follows: 1.5-7.5 g polyethylene glycol, 0.3-1.5 g zero-valent iron powder, 0.3-1.5 g NaOH, 0.4-2 mL H_2O, 10 mL real-waste transformer oil, and 360 s MW irradiation.

The results showed that the PCBs destruction efficiency in the presence of various reactants increased by adding the MW power, as shown in Figure 2.

The recorded temperatures in the reactor (after the end of MW irradiation phase) showed that in all courses, the reactions temperatures were almost approximately 90°C-110°C. The boiling rate of solution was more in higher powers, in comparison to lower powers, and its boiling time was shorter as well.

In Table 1, the negative effect of water on keeping the reactor temperature low and decreasing PCB destruction confirmed by comparing two courses of reactions in the presence and absence of water. The optimum amounts of variables were determined via initial stage of experiments by using CCD method; their amounts were as follows: 800 W power, 5.4 g PEG, 1.13 g NaOH, 0.6 g Fe, and 0.8 mL H_2O. When variable optimum amounts were used, almost 99.48% of aroclor 1262 was destroyed at reaction time of 2 min, whereas in 10 min more than 99.97% of them were destroyed.

In this investigation, five levels of variables (namely Microwave Power, PEG, NaOH, zero-valent iron, and H_2O) were selected and added to 10 mL of waste oil whose effects were specified through CCD method, simultaneously [Figure 2].

It can be clearly seen that adding PEG (1.5-7.5 g) and NaOH (0.3-1.5 g) effectively raised the decomposition efficiency of PCBs, but adding H_2O (0.4-2 mL) obviously decreased the same. Further, adding zero-valent iron (0.3-1.5 g) almost did not affect PCBs' decomposition efficiency, as shown in Figure 2. Also, their effects were determined in the optimum amounts of factors and MW power of 800 W in 6 min [Figure 3 and Table1].

These results showed that waste oil was not an absorbent of MW, and also did not affect the efficiency of PCBs decomposition. When either PEG or NaOH were used, 26.75% and 51.44% of aroclor 1262 decomposed at reaction time of 6 min, respectively. The maximum destruction efficiencies of PCBs related to both courses PEG + NaOH and PEG + NaOH + Fe were 99.97% and 99.99%, respectively.

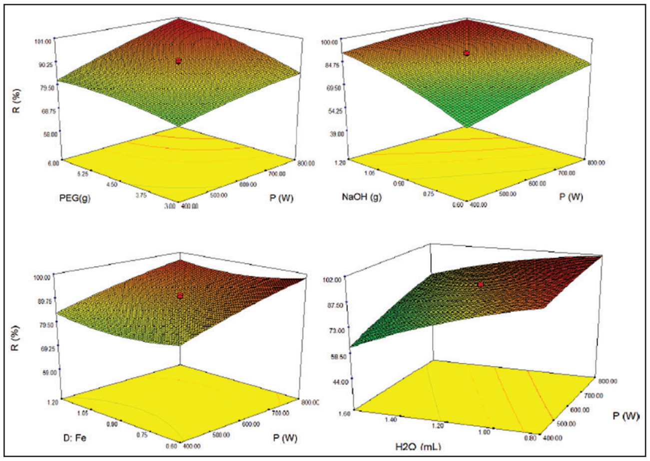

Figure 2: The influence of microwave power levels and reactants' amounts on the efficiency of PCB destruction at time 6 min (PEG: 1.5-7.5 g, NaOH: 0.3-1.5 g, Fe: 0.3-1.5 g, H2O: 0.4-2 mL, P: 200-800 W, T: 6 min)

In two of the above-mentioned runs, the reactions temperature increased to 160°C, whereas in other runs, the maximum temperature of reactions was 110°C [Table 1]. The analysis of these consequences affirmed the results of CCD method.

The destruction rate of PCBs investigated in the optimum amounts of variables in 20, 40, 60, 90, 120, 240, 360, and 600 s [Figure 4], showed that more than 99% of total PCBs were destroyed at initial 90 s of the process, and also the destruction rate of PCBs decreased after 60 s.

The investigation of aroclor 1262 destruction during the reactions indicated that the destruction kinetic was fitted with the apparent second-order kinetics, $k = 0.0001$ [Figure 5]. The destruction rate of PCBs is clearly related to initial PCBs concentration in waste oil. The results suggested that the higher chlorinated biphenyls were destroyed faster than the lower chlorinated biphenyls in all runs.

The destruction rates were as follows hierarchically: Hepta > hexa > penta; also, the destruction efficiencies of penta-, hexa- and hepta-chlorinated biphenyls at 120 s were 99.35% , 99.45%, and 99.64%, whereas at 600 s they were 99.98% , 99.98%, and 99.99%, respectively [Figure 6].

DISCUSSION

In the reactor, two main mechanisms might have occurred for PCBs' destruction. First mechanism constituted attacks to C-CL band of PCB rings by a potent nucleophilic agent, such as PEG, in alkaline environment under MW radiation. Meanwhile, NaOH acted as an activator and neutralizer of separated chloride ions of PCBs; the observation of reaction behavior showed that both PEG and NaOH are MW absorbent.[12,16,17]

Second mechanism might possibly be the production of hydrogen from the hydrothermal reaction in Fe + NaOH + H_2O system (under MW irradiation); this hydrogen might have participated in the PCBs dechlorination.

To specify the dominant mechanism, different courses were

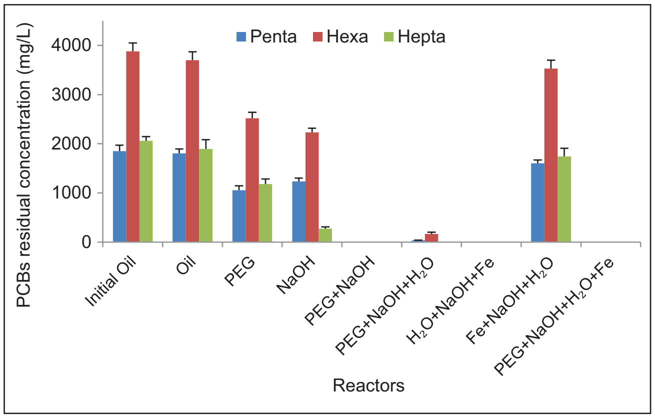

Figure 3: Variation of decomposition amount of PCBs' homological groups by MW in the optimum amounts of variables (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W, T: 6 min)

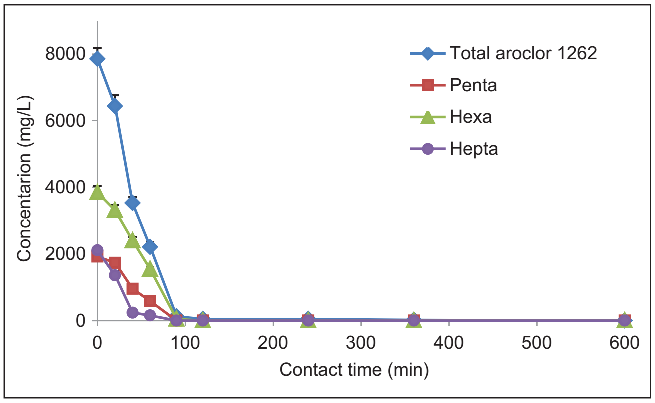

Figure 4: Residual concentration of special PCBs in the end of reaction in optimum amounts of variables (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W)

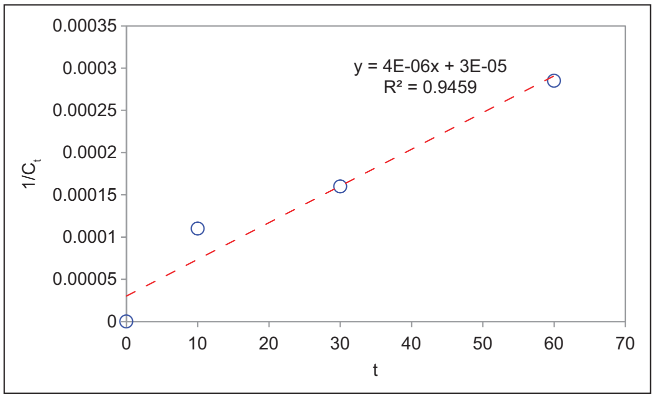

Figure 5: The decomposition kinetic of aroclor 1262 in the optimum amount of variables by MW (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W)

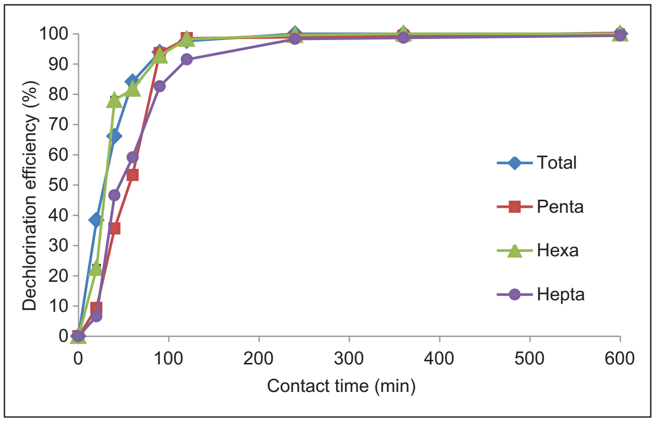

Figure 6: The decomposition efficiency of special PCBs and total aroclor 1262 in the optimum amount of variables by MW (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W)

carried out in the optimum amounts of variables [Table 1]. The results showed that when a mixture of reactants, that is, Fe, NaOH, and H_2O is used, 11.3% of PCBs were decomposed, whereas in the presence of only NaOH, 51.44% of PCBs were decomposed, which is suggestive of the fact that hydrothermal reaction had not occurred. Although, the production of hydrogen from the hydrothermal oxidation of iron in Fe + NaOH + H_2O system at temperatures above 300°C is proved in other reports, low temperature in these reactions (110°C) caused the occurrence of this mechanism to be almost impossible.[18,19] The reactor temperature was kept between 90°C and 110°C due to the evaporation and condensation of water, and then its returning to the reactor.

Also, X-ray diffraction pattern of the remnant iron powder at the end of the process indicated that Fe_3O_4 and $2NaFeO_2$ were not produced in the reactions [Figure 7]. But the first mechanism (the mixture of NaOH and PEG) clearly had the highest effect on PCBs destruction in real-waste transformer oil. The results exhibited that when a mixture of reactants including PEG1000, NaOH, and Fe is used, the reactor temperature raised and a high percentage of PCBs (99.99%) were destroyed. Furthermore, The water mount has a negative effect on the activation of PEG, and also has a negative effect on reactions temperatures.[20] These results are similar to other reports published by researchers, such as Kastanek and Liu.[8,11]

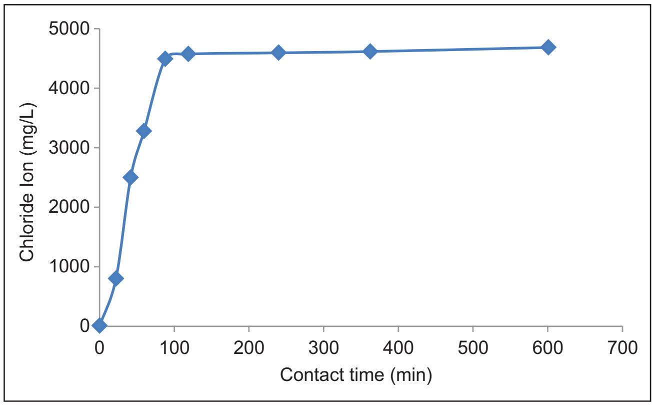

Figure 7: X-ray diffraction pattern of the remnant iron powder at the end of the process

Zero-valent iron had a low impact (<0.02%) on PCBs decomposition in the absence of water. In this course, zero-valent iron, as a catalyzer, has probably increased the destruction efficiency of PCBs, especially in higher chlorinated biphenyls. As mentioned above, the mixture of PEG and NaOH was the main factor in the destruction of PCBs. The obtained results of this process are in agreement with other previous findings.[21,22] The GC/MS chromatograms of treated oil indicated that biphenyl rings were not found in it. Aryl polyethylene glycol was the final product in these reactions that their toxicity is much lower of initial PCBs. Hence, there is a high probability of dechlorination and destruction of PCBs rings and production of aryl polyethylene glycol occurring, simultaneously.

The chlorine balance mass can reveal important information about PCBs destruction.[23] The chlorine balance mass chart illustrates that the initial organic chlorine during the process was converted to inorganic chlorine ions after 10 min of MW irradiation. Studying the chlorine mass balance proved that the destruction of PCBs during the reaction was via dechlorination, not through other ways [Figure 8]. It is also illustrated that toxic chlorinated byproducts were not produced. The GC/MS chromatograms showed that

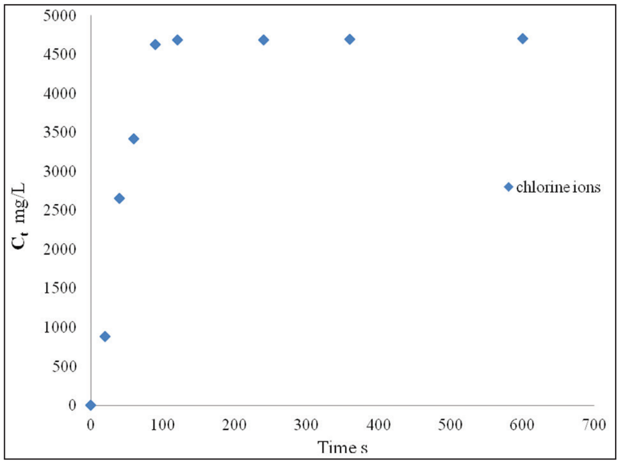

Figure 8: Resealed chloride ions during the destruction of aroclor 1262 with optimum variables by MW after of process (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W) (*P* value ≤ 0.05).

Table 1: The influence of the temperature and variables on PCB decomposition efficiency in the presence of optimum amounts of the reactants (PEG: 5.4 g, NaOH: 1.13 g, Fe: 0.6 g, H2O: 0.8 mL, P: 800 W, T: 6 min)

Runs	Kinds of reactants in variation	Destruction efficiency %				T °C
		Penta	Hexa	Hepta	Total PCBs or aroclor 1262	
1	Oil	3.6	4.82	7.47	5.23±0.2	60-70
2	PEG	41.96	34.66	40.44	26.75±1.03	120-160
3	NaOH	33.81	42.2	84.67	51.44±2.23	120-160
4	PEG + NaOH	99.98	99.97	100	99.97±0.02	120-160
5	PEG + NaOH+H_2O	97.76	95.05	99.56	96.77±0.02	90-110
6	PEG + NaOH	100	99.99	100	99.99±0.004	120-160
7	H_2O + NaOH+Fe	13.14	9.98	12.25	11.3±0.13	90-110
8	PEG+ NaOH + H_2O +Fe	99.57	99.68	99.71	99.65±0.05	90-110

hazardous chlorinated organic byproducts, such as dioxin, were not created in the process.

Previous investigations did not confirm the creation of hazardous byproducts in the presence of the above variables, in various reactions, under MW or conventional heating.[20,24] But research is still open for investigating the production of hazardous intermediates in the process. High efficiency, short time of reaction, easy recycling of waste oil, and low cost were important advantages of the suggested process for destruction of PCBs and treatment waste oil on site.

CONCLUSION

In this study, PCBs destruction in real-waste transformer oil was investigated using different kinds of variables, such PEG, NaOH, iron powder, H_2O, and MW radiation. MW radiation, PEG, and NaOH were the main reactants leading to increase of destruction efficiency. The amounts of other reactants, namely, zero-valent iron powder and H_2O, had no significant effect.

These reactants are inexpensive and available with high efficiency and short reaction time; easy recycling procedure of waste oil and low cost were other important advantages of the process. In further works, this approach can be applied for the destruction of PCBs and recycling of real waste oil and other Persistent organic pollutants (POPs) containing wastes.

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Conflicts of interest

There are no conflicts of interest.

REFERENCES

1. Hutzinger O, Safe S, Zitko V. The chemistry of PCBs. Boca Raton: CRC Press; 1974.
2. Piersol P. The evaluation of mobile and stationary facilities for the destruction of PCBs. Canada: Minister of Supply and Services; 1989.
3. Tanabe S. PCB problems in the future: Foresight from current knowledge. Environ Pollut 1988;50:5-28.
4. Safe SH. Polychlorinated biphenyls (PCBs): Environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit Rev Toxicol 1994;24:87-149.
5. Kim K, Kim K, Son SH, Chob J, Kim YC. Supercritical water oxidation of transformer oil contaminated with PCBs-A road to commercial plant from bench-scale facility. J Supercritical Fluids 2011;58:121-30.
6. Kim YC, Yook SH, Park GH, Kim K, Son SH, Supercritical water oxidation of transformer oil contaminated with polychlorinated biphenyls. J Korea Soc Waste Manage 2006;23:139-45.
7. Kastánek F, Kastánek P. Combined decontamination processes for wastes containing PCBs. J Hazard Mater 2005;117:185-205.
8. Liu X, Zhao W, Sun K, Zhang G, Zhao Y. Dechlorination of PCBs in the simulative transformer oil by microwave-hydrothermal reaction with zero-valent iron involved. Chemosphere 2011;82:773-7.
9. UNEP B. The technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls (PCB), Polychlorinated terphenyls (PCT), and Polybrominated biphenyls (PBB). UNEP/CHW/OEWG/3/INF/7/Add.1. Lead country Canada, 2004.
10. Charles Jr UP, Jinbao H. Dechlorination of PCBs, CAHs, herbicides and pesticides neat and in soils at 25 1C using Na/NH3. J Hazardous Mater 2002;92:51-62.
11. Kastanek P, Kastanek F, Hajek M, Sobek J, Solcova O. Dechlorination of PCBs by nucleofile reactants at the presence of ionic liquids and under application of microwaves. Global Nest J 2011;13:59-64.
12. Dioxin Treatment Technologies, Background Paper. U.S. Environmental Protection Agency, Office of Technology Assessment, Washington, DC, November 1991.
13. Uchida S, Kashiwagi H, Sato T, Okuwaki A, Formation of iron oxides by the oxidation of iron in Fe-MOH-H2O and Fe-MOH-H2O-O2 systems (M= Li, Na, K). J Mater Sci 1996;31:3827-30.
14. Kim KS, Hirai Y, Kato M, Urano K, Masunaga S. Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). Chemosphere 2004;55:539-53.
15. Trifan A, Calinescu I. Microwave assisted catalytic dechlorination of PCB. U.P.B. Sci Bull Series B 2009;71-80.
16. Ryoo KS, Byun SH, Choi J, Hong YP, Ryu YT, Song JS, *et al.* Destruction and removal of PCBs in waste transformer oil by a chemical dechlorination process. Bull Korean Chem Soc 2007;28:520.
17. Ukisu Y. Complete dechlorination of DDT and its metabolites in an alcohol mixture using NaOH and Pd/C catalyst. J Hazard Mater 2008;152:287-92.
18. Chuang FW, Larson RA, Wessman MS. Zero-valent iron-promoted dechlorination of polychlorinated biphenyls. Environ Sci Technol 1995;29:2460-3.
19. Chang FC, Chiu TC, Yen JH, Wang YS. Dechlorination pathways of ortho-substituted PCBs by UV irradiation in n-hexane and their correlation to the charge distribution on carbon atom. Chemosphere 2003;51:775-84.
20. Taylor ML, Wentz JA, Dosani MA, Gallagher W, Greber JS. Treating chlorinated wastes with the KPEG Process. United States: Environmental Protection Agency(EPA); 1990.
21. Kastanek P, Kastanek F, Hajek M, Sobek J, Solcova O. Dehalogenation of polychlorinated biphenyls (PCB) by nucleofile reactants at the presence of ionic liquids and under application of microwaves. Global Nest J 2011;13:59-64.
22. Cafissi A, Beduschi S, Balacco V, Sacchi B, Trasatti S. Chemical dechlorination of polychlorinated biphenyls (PCBs) from dielectric oils. Environ Chem Lett 2007;5:101-6.
23. Cynthia GJ, Joseph S, Mohamad AP, Dianne LP. Dechlorination of polychlorinated biphenyls in industrial transformer oil by radiolytic and photolytic methods. Environ Sci Technol 2003;37:5773-7.
24. Kyeongsook K, KwangSin K, Hwan SS, Jungho C, Cheol KY. Supercritical water oxidation of transformer oil contaminated with PCBs-A road to commercial plant from bench-scale facility. J Supercrit Fluids 2011;58:121-30.