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Dechlorination of Polychlorinated Biphenyls in Real Waste Transformer Oil Using a Modified Household Microwave Oven in Presence of Sodium Hydroxide and Polyethylene Glycol

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ABSTRACT

This research was carried out to assess the dechlorination and decomposition of Polychlorinated biphenyls (PCBs) in the real waste transformer oil using polyethylene glycol 1000/NaOH through a modified household microwave oven. To do so, the influence of polyethylene glycol (PEG) (1.5-7.5 g) and NaOH (0.3-1.5 g) under microwave (MW) power of 500 W on the dechlorination efficiency of PCBs, existed in real waste transformer oil, was investigated. The results showed that by increasing the PEG 1000 (1.5- 7.5g) and NaOH (0.3-1.5g) amounts, the dechlorination efficiency of PCBs increased from 35 to 99.99% under MV power of 500 W for the reaction time of 6 min. The optimum amounts of PEG and NaOH were 5 g and 1 g, respectively. The results indicated that the PCBs dechlorination rate followed first-order kinetic (k = 0.019, R^2 = 0.91), and more than 90% of total PCBs were dechlorinated at the first 90 seconds of the reaction. After 90 seconds, the dechlorination rate decreased. Accordingly, results showed that MW has extraordinary influence on PCBs decomposition from waste transformer oil, and the reaction time substantially decreased compared to conventional heating.

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1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are derivatives of biphenyls in which two to ten chlorine ions have replaced hydrogen atoms on two biphenyl rings [1]. Due to their extremely high chemical and thermal stabilities and electrical insulating properties, they have been used for a wide variety of commercial applications, such as dielectric fluids in transformers and capacitors, heat transfer and hydraulic systems, sealants, plastics and electromagnets [2]. These chemicals were produced in great quantities in the 1960s, their physicochemical resistance to destruction by acids, bases, heat, and hydrolysis have led to long term environmental contaminations [3]. PCBs production and use became forbidden or limited in the late 1970s [4]. Although the production of PCBs is banned in all countries, they have still remained in large quantities in transformers and capacitors and in waste oils storage sites [5].

As a part of Stockholm agreement by the United Nations Environment Program [6] on May 17, 2005, application and use of transformer oils with PCB concentrations exceeding the regulatory limit (2 ppm) must be followed by their proper disposal [5].

A variety of approaches have been used for disposal of PCBs; among which the most usual approach is incineration technology that is wholly effective for decomposition of PCBs, however, it may produce highly toxic by-products via flue gas stream [7].

Other approaches involve base catalyzed decomposition (BCD), paralysis, supercritical water oxidation, plasma arc decomposition, sodium reduction,

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super-critical water oxidation (SCWO), KPEG method and etc [8, 9].

Due to simplicity of KPEG method, it has been accepted as a proper technology to destruct PCBs. In this method, polyethylene glycol and alkali are used for destruction of PCBs. Use of available and cheap materials is the main advantage of this method, but its long reaction time impedes its application in the destruction of PCBs [10]. In this field, Sabata et al. [11] studied the destruction of PCBs in the waste oil using PEG, KOH and conventional heating; they found that PCBs removal efficiency with mass ratios of PCB/PEG/KOH (1/30.25/15.12), temperature of 160 ^{o}C, and reaction time of 225 min reached to 98.7%. Subsequently, Kwon et al. [3] investigated the chemical removal of PCBs in waste oil in the presence of PEG600, KOH, and Al and found that under the experimental conditions of PEG600/KOH/Al/150°C/4h, average removal efficiency of PCBs reached 99.99%.

In recent years, microwave (MW) heating, as an innovative approach, has been used for the destruction of chlorinated organic pollutants with fast reaction rate and high removal efficiencies instead of conventional heating [12-14]. With ion migration and dipolar polarization, the dielectric molecules in the solution under MV irradiation can be vibrated and subsequently heated to high temperature in a very short time (15). The heat reduces activation energy of the reactions, and undermines the chemical bond intensities of various molecules [15].

In this field, Man et al. [16] proved that MW heating, compared to conventional heating, accelerated the destruction rate of the chlorinated compounds. Liu et al. [17] also found that MW irradiation could affect the decomposition of pentachlorophenols which are adsorbed on granular activated carbon.

The objective of this study was to combine the high reactivity of polyethylene glycol and NaOH under MW radiation for the dechlorination of PCBs in real waste transformer oil at low reaction time. PEG as a potent nucleophilic agent and NaOH as a reaction activator and also a neutralizer of separated chloride ions were used for PCBs dechlorinating in waste oil, under MW radiation. The influence of MW irradiation, the amount of PEG and NaOH on removal efficiency of PCBs was investigated as well.

2. MATERIAL AND METHOD

2. 1. Material   Waste transformer oil containing PCBs was obtained from a waste oil storage site in south of Iran. The waste oil contained 31 kinds of PCBs including two, three, four, five, six and seven chlorinated PCBs (No's 8, 28, 37, 44, 49, 52, 66, 70, 74, 77, 82, 87, 99, 105, 114, 118, 126, 128, 138, 153, 156, 158, 169, 170, 179, 180, 183, 187 and 189). The
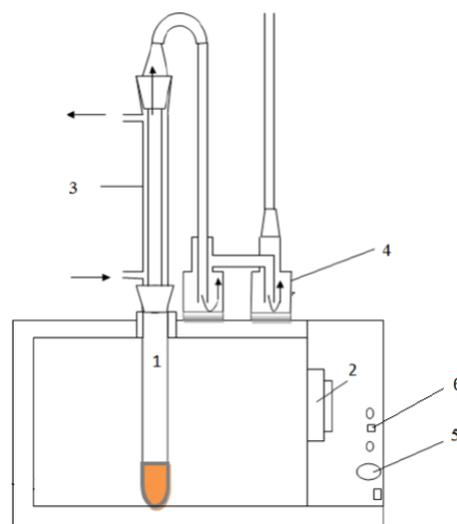
concentration of total PCBs, which was determined prior to the process, was 8534 mg/L (containing 1.4 mg/L di-, 171.6 mg/L tri-, 537.6 mg/L tetra-, 1902.8 mg/L penta-, 3856.3 mg/L hexa and 2074.9 hepta-chlorinated biphenyls).

Required chemical materials for the experiments including Polyethylene glycol (PEG1000), NaOH (with 97% purity) and n-hexane with analytical grade were purchased from Merck (Darmstadt Germany).

2. 2. Method   A modified domestic microwave oven (Delonghi Company) operated at 2450MHz with a maximum power of 1000 W was used for generating MV heating. It was modified by installing a condensing system above the reactor for preventing liquid evaporation (Figure 1). Above the oven a hole with 35 mm diameter was opened from which a quartz batch reactor (30 mm, i.d.) was inserted into the MV oven. The top part of the reactor was connected to a condensing system for collecting distillation, and so the created gas could pass via two bottles containing n-hexane, which were connected in series.

After the reaction, the processed oil was cooled to 6 ^{o}C, and then mixed with n-hexane in bottles for PCB detection. All these experiments were carried out in batch reactor; only the main effective factors (PEG and NaOH) were tested for PCBs destruction of waste transformer oil.

PEG as a potent nucleophilic agent was used for chlorine elimination from PCB rings in waste oil under alkaline condition. Solid NaOH, as an activator and neutralizer of separated chloride ions, was utilized in various conditions of this process.

Figure 1. Schematic representation of experimental set up; 1. quartz reactor; 2.   MV lamp; 3. condenser; 4. vessels containing hexane; 5. switch control; 6. IR-temperature sensor

During the process the power of the MV field was 500 W; polyethylene glycol amounts were 1.5 to 7.5 g, and NaOH amounts were between 0.3-1.5 g in all tests. These variables were selected based on previous studies and our initial experiments results. The amount of waste oil used in all experiments was 10 ml.

The MV schedule was regulated for one minute irradiation and two minutes cooling process, recurrently. The total reaction time was 16 min, including MV irradiation time or reaction time (6 min) and the break time for reactor cooling (10 min).

The MV schedule was determined in the initial experiments. Afterward, the optimum amounts of variables were determined, and the reactions rates were investigated ranging from 0 to 360 s.

Two or sometimes three samples were analyzed in every stage. Samples were analyzed using AGILENT Gas chromatograph 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 treated oil at the end of the process (1/40).

The type of column was DB-5, capillary, length 30m, diameter 0.32m, and film thickness 0.25μm. The injector and detector temperatures were at 270 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 following: initial temperature 120 °C; the temperature increased at the rate of 15 °C/min to 210 °C and kept constant for 1 min; the second increase rate was 20 °C/min to 240 °C which was fixed for 2 min; and the third one was 30 °C/min to 295 °C for 2 min. The PCBs calibration curve was obtained by injecting pre-determined concentrations to GC/ECD.

A VARIAN 4000 GC/MS was implemented for recognition of the PCBs destruction by-products. Capillary column and carrier gas were DB-5 MS and helium, respectively.

3. RESULT AND DISCUSSION

In this work, the effects of PEG and NaOH under MV irradiation were studied for removal of PCBs in transformer oil at the reaction time of 6 min. PEG was used as a nucleophile material, under MV irradiation, which attacks carbons with positive charge on the benzene rings, resulting the chlorine ions to be separated from benzene rings. Then, the separated chlorine ions from benzene rings react with NaOH and produce NaCl, thereby, neutralize chlorine ions.
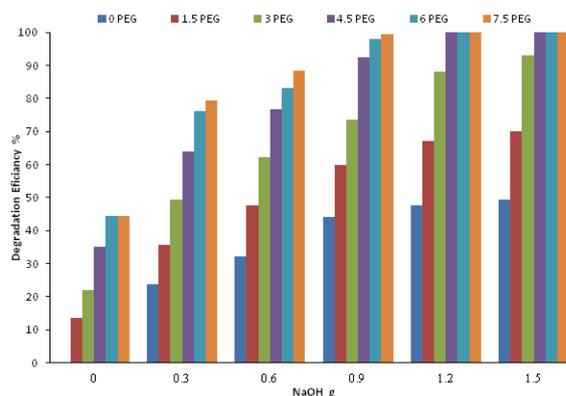
Results show that with increasing PEG dosage from 1.5 to 7.5 g, PCB decomposition efficiency increased from 10 to 41%, respectively. On the other hand, with increasing NaOH dosage form 0.3 to 1.5 g, the PCB decomposition efficiency increased from 16 to 45%.

Also, with simultaneous increase of PEG (1.5 to 7.5 g) and NaOH (0.3 to 1.5 g) dosages, the dechlorination efficiency of PCBs increased from 35 to 99.99% under MV radiation at the reaction time of 6 min.
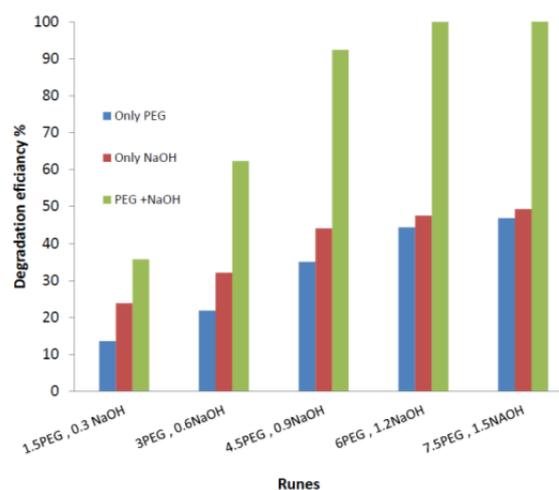
Consequently, in this study the synergetic effect of PEG and NaOH in the dechlorination of PCBs was 15%. Meanwhile, the higher dosages of PEG and NaOH had a slight increase in the PCB removal efficiency (Figures 2 and 3).

When PEG was used for dechlorination of PCBs alone, chlorine ions accumulated in the reactor, thereby, prevented the higher activation of PEG and decreased PCBs removal efficiency (Equation (1)). The PCB decomposition efficiency increased to 45% when only NaOH was used in the reactor.

It is higher than the time that PEG alone was used (Figure 3); this is related to the reaction of NaOH with chlorine ions.

Figure 2. PEG influence, in the presence of NaOH, on the dechlorination of PCBs in waste oil by MV power of 500W after 6 min
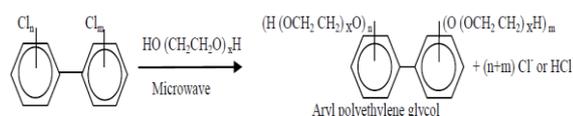
Figure 3. NaOH influence, in the presence of PEG, on the dechlorination of PCBs in waste oil under MV power of 500W after 6 min

Due to irradiation of MV and ionization of NaOH, these reaction rates were very high. In this reaction, the hydroxide ions (OH⁻) were replaced with chlorine ions in benzene rings and produced biphenyl alcohol. Also, sodium ions were reacted with chlorine ions and produced NaCl; thereby, decreased the chlorine ions concentration in reactor (Equation (2)).
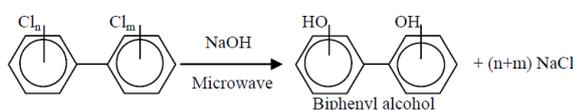
While with adding PEG in the presence of NaOH, sodium PEG alkoxide was generated that can phase transfer itself into the organic phase via self-complexation and as a potent nocleophile that can attack carbons in PCBs with the positive charge. As a consequence, the chlorine ions were neutralized, the PEG activation for attacking the positive charged carbons rose, and PCBs removal efficiency increased (Equation (3)) [18]. These results are similar to the reports published by other researchers such as Ryoo and Kastanek and Kastanek [3, 11].

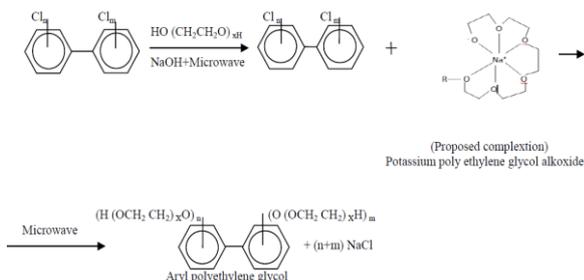The suggested dechlorination pathways of BCBs are as follows:

Equation (1): When PEG is used for dechlorination of PCBs alone:

Equation (2): When NaOH is used for dechlorination of PCBs alone:

Equation (3): When PEG and NaOH are used for dechlorination of PCBs:

The optimum dosages of NaOH and PEG were determined by considering the maximum removal efficiency of PCBs and minimum consumption of them. The optimum condition was obtained in the PEG and NaOH dosages of 5 g and 1 g, respectively, at the reaction time of 6 min.
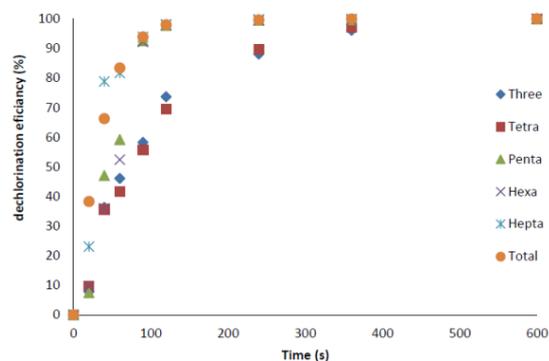
At the optimum condition, PCBs dechlorination efficiency was up to 99.9% which is shown in Figures 2 and 3. The dechlorination rate was additionally investigated for the optimum amounts of PEG and NaOH in 20, 40, 60, 90, 120, 240, 360 and 600 seconds.
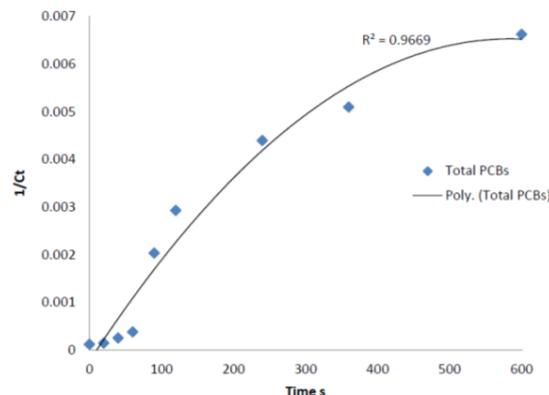
The results indicated that more than 80% of total PCBs were dechlorinated at the first 60 second of the reaction time. Also after 90 second, the dechlorination rate decreased (Figure 4). The PCBs dechlorination results in this process were fitted to first-order kinetic (k = 0.019) (Figure 5).

The results illustrated that dechlorination rates in the higher chlorinated biphenyls (as penta-, hexa- and hepta-chlorinated biphenyls), were higher than lower chlorinated biphenyls (three- and tetra-chlorinated biphenyls) in all courses. The number and position of chlorine ions on biphenyls rings and the symmetry and asymmetry of molecule are main factors affecting the resistance of PCBs to decomposition. Small number and ortho position of chlorine ions on biphenyls rings and symmetry of molecules increase the resistance of PCBs to decomposition [18].

The resistance of tetra chlorinated biphenyls to decomposition was almost equal to three chlorinated biphenyls, due to higher concentration of PCB52 (as a tetra chlorinated biphenyls) in waste oil. PCB52 has a symmetric structure and is resistant to decomposition, as shown in Figure 6.

Figure 4. Decomposition efficiency of special PCBs and total PCBs by MW (P=500 W, PEG=5 g, NaOH=1 g)

Figure 5. The dechlorination kinetic of PCBs in the optimum amount of variables by MW (PEG=5 g, NaOH= 1 g, P=500W)

Finally, the results showed that almost 100% of PCBs were dechlorinated in this process at reaction time of 10 min under MW. To reach this efficiency, decomposition with conventional heating needs 120 min in similar condition; therefore, it is about 10 times higher than the MW heating. These results are similar to the reports published by Gedy et al. [19] that showed, MV irradiation enhance the reaction rate of 10 to 1200 times compared to conventional heading.

To determine segregated chloride ions of PCBs at the end of the process, the segregated chloride ions of PCBs and PEG were separated by precipitation at the bottom of the reactor and identified by ion chromatography. The results of mass balance of chloride ions showed the total organic chlorine ions which were converted to mineral chlorine during dechlorination reaction under MV radiation in 10 min (Figure 7). It indicates that hazardous byproducts, containing chlorine ions, were not produced [20, 21].

The observation of reaction behavior in the control samples, without NaOH and PEG, showed that increasing the temperature, the boiling of solution and the dechlorination of PCBs in waste oil under MW irradiation did not happen.

It indicates that the real waste oil absorbance of MW radiation is negligible. Therefore, MW irradiation alone is not able to decompose PCBs in the real oil. In the presence of only PEG, at the end of the reaction, aryl polyethylene glycol was produced and precipitated with PEG at the bottom of the reactor.

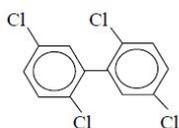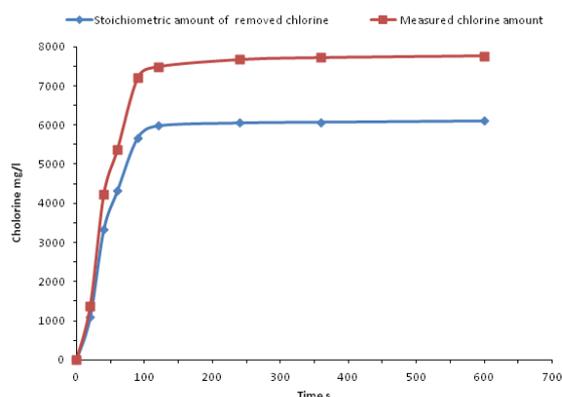The investigations carried out by EPA with conventional heating on PCBs decholorination showed

that the produced mixture of the aryl polyethylene glycol at the end of reaction were neither toxic nor mutagenic to various animals [18].

Polychlorobiphenyl alcohol and biphenyl alcohols were produced in the presence of NaOH alone, at the end of the reaction. These compounds are soluble in oil and can act as a precursor of poly chloro dibenzofurans (PCDF) production [18, 22]. Therefore, it is suggested not to use NaOH alone for PCB dechlorination.

In the presence of NaOH and PEG, aryl polyethylene glycol and possibly a negligible amount of poly chlorobiphenyl alcohol are final products of this process under MW radiation after of 10 min. These mixtures have much lower toxicity than PCBs in a way that the aryl polyethylene glycol product is about 300 times less reactive than starting PCBs [18, 22]. Of course, research is still open for possible creation of hazardous intermediates under MV radiation.

6. CONLUSION

In this study, the PCBs dechlorination from real waste transformer oil was investigated using PEG, NaOH and MW radiation. Results showed that PEG and NaOH under MW radiation had extraordinary influence on PCBs dechlorination in real waste transformer oil.

The selected reactants (PEG, NaOH) are inexpensive and available, and have high efficiency and short reaction time. Waste oil easy recycling procedure and simple operation are other important advantages of this process. This method can be applied for dechlorination of PCBs and recycling of real waste oil and other POPs-containing wastes in further works

Figure 6. Structure of PCB52

Figure 7. Produced chloride ions from dechlorination of PCBs by MW at the end of the process at various times

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چکیده

در این تحقیق از یک دستگاه ماکروویو خانگی اصلاح شده و پلی اتیلن گلیکول ۱۰۰۰ و سود برای کلر زدای و تخریب پلی کلرو بیفنیل های موجود در روغن زائد واقعی ترانسفورماتور استفاده شد. همچنین، تأثیر پلی اتیلن گلیکول (۱/۵–۷/۵ گرم) و هیدرواکسید سدیم (۰/۳–۱/۵ گرم) روی راندمان کلر زدایی از پلی کلرو بیفنیل های موجود در روغن زائد واقعی ترانسفور ماتور تحت تابش ماکروویو با توان ثابت ۵۰۰وات بررسی شد. نتایج نشان داد راندمان کلر زدایی از PCBها، با افزایش مقادیر پلی اتیلن گلیکول(۱/۵–۷/۵ گرم) و سود (۰/۳– ۱/۵ گرم) تحت تابش ماکروویو ۵۰۰ وات و محدوده زمان واکنش ۶ دقیقه، ۳۵٪ تا ۹۹/۹۹٪ افزایش داشت. مقادیر بهینه PEG و NaOH به ترتیب ۵ گرم و یک گرم شد. همچنین، نتایج نشان داد که سرعت کلر زدایی از PCB ها مطابق با کنتیک با کنتیک درجه اول است (۰/۰۱۹ = k, R^2 = ۰/۹۱) و در محدوده زمانی ۹۰ ثانیه ابتدای فرایند، بیش از ۹۰درصد از PCBها کلر زدایی شدند و بعد از ۹۰ ثانیه، سرعت کلر زدایی کاهش داشت. مطابق با نتایج این مطالعه، تابش ماکروویو در مقایسه با گرمای متداول تأثیر چشمگیری بر فرایند کلر زدایی از PCBهای موجود در روغن ترانسفور ماتور و کاهش زمان آن داشته است.

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