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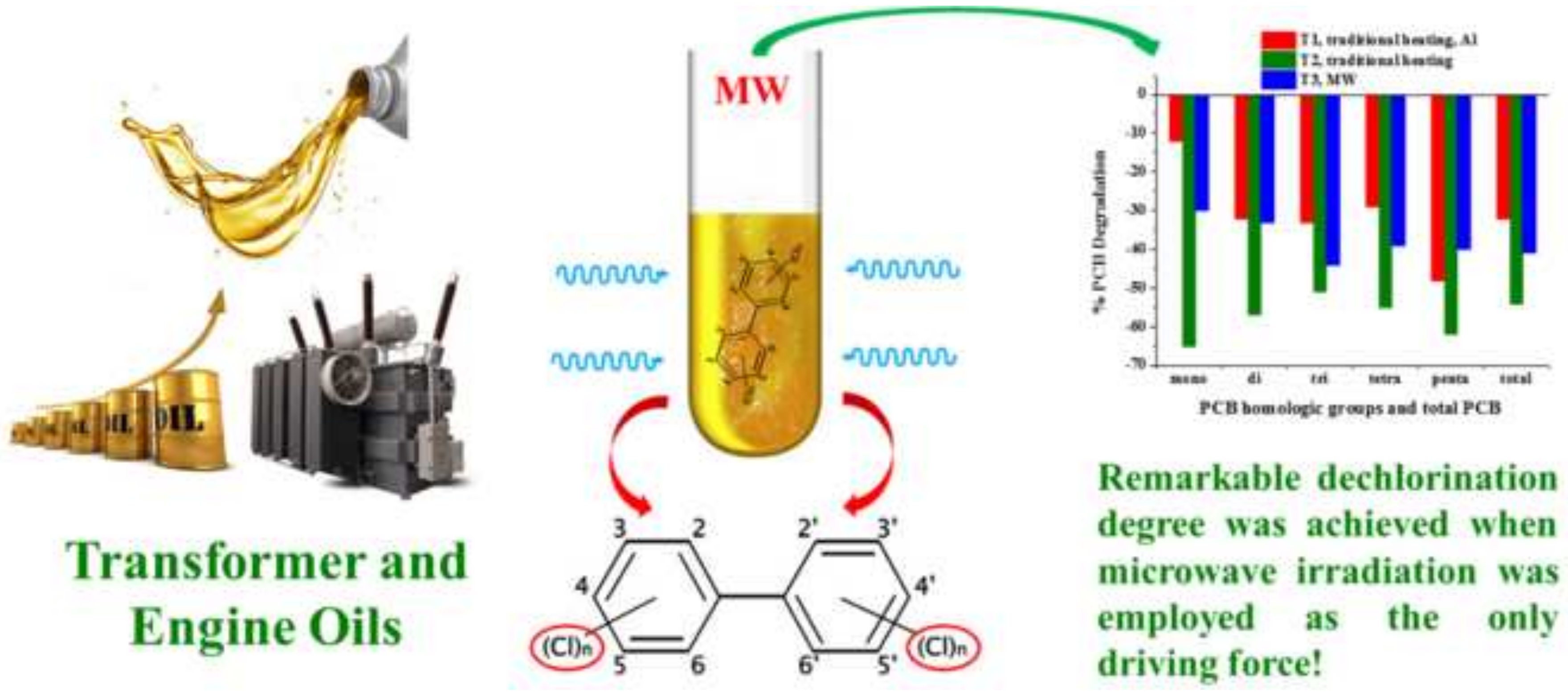
Graphical Abstract



Remarkable dechlorination degree was achieved when microwave irradiation was employed as the only driving force!

Abstract

The removal of polychlorinated biphenyls (PCBs) both from siloxane transformer oil and hydrocarbon engine oil was investigated through the application of microwave (MW) irradiation and a reaction system based on polyethyleneglycol (PEG) and potassium hydroxide. The influence of the main reaction parameters (MW irradiation time, molecular weight of PEG, amount of added reactants and temperature) on the dechlorination behavior was studied. Promising performances were reached, allowing about 50 % of dechlorination under the best experimental conditions, together time and energy saving compared to conventional heating systems. Moreover, an interesting dechlorination degree (up to 32 %) was achieved for siloxane transformer oil when MW irradiation was employed as the unique driving force. To the best of our knowledge, this is the first time in which MW irradiation is tested as the single driving force for the dechlorination of these two types of PCB-contaminated oils.

Application of microwave irradiation for the removal of polychlorinated biphenyls from siloxane transformer and hydrocarbon engine oils

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Abstract

The removal of polychlorinated biphenyls (PCBs) both from siloxane transformer oil and hydrocarbon engine oil was investigated through the application of microwave (MW) irradiation and a reaction system based on polyethyleneglycol (PEG) and potassium hydroxide. The influence of the main reaction parameters (MW irradiation time, molecular weight of PEG, amount of added reactants and temperature) on the dechlorination behavior was studied. Promising performances were reached, allowing about 50 % of dechlorination under the best experimental conditions, together time and energy saving compared to conventional heating systems. Moreover, an interesting dechlorination degree (up to 32 %) was achieved for siloxane transformer oil when MW irradiation was employed as the unique driving force. To the best of our knowledge, this is the first time in which MW irradiation is tested as the single driving force for the dechlorination of these two types of PCB-contaminated oils.

Keywords: microwave, PCBs, dechlorination, transformer oil, engine oil.

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1. Introduction

Since the late 1920, polychlorinated biphenyls (PCBs) have been used in a wide variety of applications thanks to their specific properties (Ivanov and Sandell, 1992). Unfortunately, these compounds are toxic and persistent pollutants that threaten not only the environment but also the human health (Wang D.G. et al., 2008) and due to their lipophilic nature, they can bio-accumulate in cells up to the food chain. Today, the production of PCBs has been banned all over the world, but there are many residual devices containing these compounds, such as transformer and engine oils, whose improper management practices can cause serious problems, making urgent their replacement and their proper disposal. However, the decontamination of oils from PCBs in electrical devices is extremely difficult and also the replacement of the contaminated oil with a new one is not a feasible solution because PCBs remain absorbed on electrical coils and layers of magnetic material, making impossible their complete removal, thus causing the inevitable contamination even of the new oil. Until now, the only proven and widely used technology for treating big amounts of polluted matrices is their incineration which can destroy over 99.9999 % of PCBs (Liu et al., 2011). However, there is a widespread public opposition to this approach due to the potential release of Cl_2, HCl and polychlorinated dibenzo-p-dioxins and dibenzofurans via flue gas stream (Davila et al., 1994). In order to overcome these problems, a patented method (Tumiatti, 1997), industrially employed, removes PCBs from different oils in the presence of polyethylene/polyalkylene glycols characterized by high molecular weight, hydroxides or alkali alcoholates and non-alkali metals working around 200°C. Two different degradation pathways may occur, the nucleophilic substitution and the hydrodechlorination. In fact, the first mechanism is typical of the polyethyleglycol/polyalkyleneglycols-base process where polyethylenglycolate, formed as a base is added to PEG, selectively attacks the active sites (halogen groups) of the polychlorobiphenyl molecule. In addition, according to this pathway, PEG also acts as phase transfer catalyst due to its high lipophilicity, moving polychlorobiphenyl molecules from the apolar phase (oil) to the polar one (PEG/base) where the reaction does occur. The second mechanism (hydrodechlorination) is attributed to the presence of metal catalyst and hydrogen donors, enhancing the hydrodechlorination of PCBs. The industrially adopted method allows good removal yields but requires long reaction times, up to 2 h (Tumiatti, 1997). More recently, other approaches have been developed for remediation of PCBs, such as thermal, oxidative, reductive photocatalytic and microbial technologies (Beless et al., 2014; Borja et al., 2005; De Filippis et al., 1997; Field and Sierra-Alverez, 2008; Habekost and Aristov, 2012; Jelic et al., 2015; Kanbe and Shibuya, 2001; Kume et al., 2008; O'Brien et al., 2005; Ohbayashi et al., 2002; Ohmura et al., 2007; Peng et al., 2014; Rastogi et al., 2009; Seok et al., 2005; Shaban et al., 2016; Van Aken and Bhalla, 2001; Villalobos-Maldonado et al., 2015; Wang et al., 2016; Wu et al., 2012; Wu et al., 2005; Yao et al., 2014; Zhao et al., 2015). In addition to these techniques, also microwave irradiation (MW) has been investigated due to its advantages ascertained in many different applications (Abramovitch et al, 1999a, 1999b, 1998; Cravotto et al., 2007; Huang et al., 2011; Kamarehie et al., 2014; Lin et al., 2013; Liu and Yu, 2006; Liu et al., 2008; Tajik et al., 2014). In fact, in the past few years the interest in the employment of MW irradiation has considerably increased because it represents a sustainable and green tool for many applications, improving selectivity together with a significant reduction of the reaction time (often by orders of magnitude) and of energy consumption (Antonetti et al., 2015, 2012, 2010; Appleton et al., 2005; Raspolli Galletti et al., 2013, 2010, 2008). As a novel and efficient approach, MW irradiation has been especially used to treat contaminated soils, obtaining interesting results. A series of pioneer studies were reported by Abramovitch on MW irradiation for the remediation of PCBs from polluted soil in the presence of microwave absorbers (Cu_2O, graphite) and NaOH. He reported that most of the chlorinated aromatics were decomposed and the majority of the dechlorinated products were possibly mineralized into the soil (Abramovitch et al., 1999a, 1999b, 1998). Liu and Yu investigated the combined effects of MW irradiation and granular activated carbon on the removal of PCBs from soils and indicated that the addition of carbon to soil effectively increases its ability to absorb MW energy, this heating resulting in the enhanced degradation of PCBs in the soil (Liu and Yu, 2006). The employment of a MW absorber has been also studied by Huang which investigated the removal efficiency in PCB-contaminated soils by microwave irradiated MnO_2, absorber of microwave energy, obtaining a removal percentage above 95 % (Huang et al., 2011). Cravotto combined solid Fenton-like reagents (sodium percarbonate and the urea/hydrogen peroxide complex) and MW irradiation for the decomposition of organic pollutants of the soil, highlighting that 4-chloronaphthol, 2,4-dichlorophenoxyacetic acid and *p*-nonylphenol were completely degraded (Cravotto et al., 2007). On the other hand, the use of MW irradiation for the removal of PCBs from oil matrices has been less investigated (Kamarehie et al., 2014; Kastanek et al., 2011; Lin et al., 2013; Liu et al., 2011; Liu et al., 2008; Tajik et al., 2014). Liu studied the applicability of MW irradiation for the removal of PCBs from the soil heavily contaminated by capacitor oil in the presence of sodium hypophosphite, iron powder and granular activated carbon as MW-adsorbing materials. In the presence of sodium hypophosphite and carbon, about 80 % of PCBs in soils were effectively removed by MW irradiation for 10 minutes and the further addition of iron powder raised the average removal efficiency up to 95 % (Liu et al., 2008). Lin investigated also the effect of MW in the removal of PCBs from soil polluted with capacitor oil in the presence of MnO_2 as MW absorber and oxidizer. The removal efficiencies for di-, tri-, tetra-, penta-, hexa-, hepta- and octa- chlorobyphenyls were 95.9, 82.5, 52.0, 71.6, 62.5, 28.6 and 16.1 %, respectively, applying MW irradiation for 45 minutes to a mixture of MnO_2, contaminated soil and water (Lin et al., 2013). Kastanek examined the influence of MW field on the effectiveness of KPEG method (nucleophilic substitution by alkaline polyethylene glycol, PEG) in the removal of PCBs from highly contaminated mineral oils. The obtained results show that MW irradiation significantly increases the reaction rate and the method’s effectiveness. Moreover, the authors highlight that the addition of a small amount of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate markedly positively affects the results achieved under MW irradiation

(Kastanek et al., 2011). However, the paper does not deal with the influence of some important parameters on the achieved results, such as temperature, MW irradiation time, molecular weight of PEG, amount of added reactants on the effectiveness of the KPEG method. Finally, MW irradiation was employed as tool to induce the hydrothermal reaction between iron powder, NaOH and H_2O as reactants in order to produce hydrogen, responsible then for the dechlorination of PCBs. The efficiency of this method was verified on a simulated oil based on hexadecane containing 100 mg/L of Aroclor 1254, achieving the almost complete dechlorination after MW treatment for 10 minutes (Liu et al., 2011).

Now, this study investigates the efficiency of MW irradiation compared to the traditional heating and the influence of some selected reaction conditions on the removal of PCBs from two types of oils: siloxane transformer oil and hydrocarbon engine one, adopting the industrially applied reaction mixture made of PEG and potassium hydroxide in the presence or in the absence of aluminum powder. In addition, to the best of our knowledge, this is the first application in a systematic investigation of MW efficiency when applied as unique driving force in the dechlorination of these two different oil matrices, in the absence of other chemicals.

2. Material and methods

2.1 Materials

Aroclor 1242 pure (1mL neat - F109 – lotto 399-6B) was purchased from Chemservice srl (MI-Italy). PCB 19* (D), PCB 156* (D), PCB 81* (D) (50 µg/mL in toluene) were provided from Wellington Laboratories and PCB mixtures of individual congeners (PCB 525; 525.1; PCB mix. 500 µg/mL each in hexane) were obtained from Supelco and used as received. Polydimethylsiloxane transformer oil was provided from Chimica San Fedele, whereas hydrocarbon engine oils are commercial products: Q8 Formula Plus (cod. SAE 15W-40) and Q8 Formula F1 (cod. SAE 10W-50). The model polluted siloxane transformer oil sample was prepared by adding

400 µL of Aroclor 1242 in isooctane to 40 mL of the transformer oil, whereas the model hydrocarbon engine oil was prepared by adding 400 µL of Aroclor 1242 in isooctane to 40 mL of a mixture of Q8 Formula Plus and Q8 Formula F1 oils (1:1, v/v). Polyethylene glycol 8000, polyethylene glycol 200, ethylene glycol, aluminum powder, potassium hydroxide, potassium bicarbonate and hexane were purchased from Sigma Aldrich and used as received.

2.2 Methods

The MW dechlorination experiments were carried out using a commercially available mono-mode microwave unit (CEM Discover S-class system) equipped with a calibrated external infrared sensor and a PC control. The instrument consisted of a single-mode, self-tuning cavity where the correct position of the reaction vial was automatically tuned to ensure reproducible conditions at each run. The oven was operated by a continuous power generator capable of supplying an irradiation power from 0 to 300W (with 1W-step increment) with a fine and automated control of the sample temperature based on the CEM PowerMax technology. Initial reaction time (t = 0) was taken when the temperature set point was reached. Air simultaneous cooling of the sample during MW irradiation (cooling system PowerMAX) was adopted for selected runs, as specified in the text. This is a new technology which allows the simultaneous cooling of the reactor with a stream of air on the outside of the reaction vessel driving its heating with a substantial amount of microwave energy, up to 300 W. In this way, when the power is increased, it is possible to avoid the risk of overheating temperature-sensitive reactants, enabling more energy to be introduced into the reaction without the degradation of the product.

In a typical procedure, 2.5 g of the selected oil and the right amounts of chosen reagents were introduced in a 10 mL reactor equipped with a magnetic teflon stir bar. The reactor was capped and heated to the desired temperature under maximum stirring. After reaction time was over, the sample was rapidly cooled to room temperature, filtered and washed several times with hexane in order to recover the total amount of the oil for the successive PCB analysis.

Traditionally heated dechlorination reactions were performed in 50-mL two-neck round-bottom flask equipped with a condenser. In a typical procedure, 10 g of the selected oil and the selected amounts of chosen reagents were loaded in the round-bottom flask equipped with a magnetic teflon stir bar. The run was carried out at the desired temperature by heating in oil bath previously thermostated at the stated temperature. Upon completion of the reaction, the sample was quenched in a cold water bath and worked-up as reported above. For both approaches reproducibility of triplicate experiments resulted within 3 %. Detailed experimental conditions adopted in the dechlorination reaction on the siloxane transformer and hydrocarbon engine oils are reported in the Supplementary Information (see S1 and S2 respectively in the Supplementary Information).

2.3 Analysis

Before the analysis, purification of the oil samples was carried out according to the clean-up technique SPE (Solid Phase Extraction) using a column Supelco Supelclean Sulfoxide PPSPE 3g/6mL consisting of a silica-bonded sulfoxide (-SO) phase. The column was washed with acetone and then equilibrated with hexane. At the same time, the oil sample was diluted with hexane and two internal standards of PCB congener, PCB 19* and PCB 156*, were added in order to evaluate the average recovery percentages of PCBs from each oil sample during the clean-up procedure. Later, the treated sample was layered onto the upper part of the SPE column. Then, the sample was eluted with hexane and two fractions were collected for the subsequent analysis. The first one mainly includes apolar hydrocarbons, whereas the second one primarily contains polar hydrocarbons and PCBs. This second fraction was subsequently diluted to the right volume and loaded with the internal standard (PCB 81*) for the following quantitative determination. The recovery percentages of the internal standards (PCB 19* and PCB 156*) for each oil sample and the corresponding average values are reported in the Supplementary Information (see S3 in the Supplementary Information). The average values were employed for the calculation of PCB concentrations after GC-MS analysis.

Identification and quantitative analysis of PCBs and reaction media products was accomplished by a Thermo Finnigan MS Trace DSQ gas chromatography/mass spectrometry (GC-MS) equipped with a G.C. column Agilent DB5-MS Ultra Inert (column length 30 m, inner diameter 0.25 mm and thickness of the stationary phase 0.25 µm). The transport gas was helium 5.5 with a flow of 1.3 mL/min. The temperature of the injection port was set at 250 °C, carrier pressure at 100 kPa and the injection was carried out in the splitless mode. The column temperature was programmed as follows: the oven was heated at 45 °C for 3 minutes, then the temperature was raised by 30 °C/min up to 130 °C remaining at this temperature for 2 minutes, then the temperature was raised by 8 °C/min up to 250 °C and as soon as the temperature had reached the desired value, it was again raised by 30 °C/min up to 300 °C remaining at this temperature for 6 minutes.

The determination of water amount in the oil samples was carried out according to the ASTM D 6304-07 method (ASTM International, 2007).

3. Results and Discussion

3.1 Dechlorination activity adopting traditional heating

The experiments were carried out using a commercial siloxane transformer oil and a commercial hydrocarbon engine one. In preliminary experiments, we replicated PCB degradation under the reaction conditions of a patented industrial method (Tumiatti, 1997) using traditional heating at 100°C for 2 h. The reaction involves the contemporary presence of high molecular weight polyethyleglycol (PEG 8000), potassium hydroxide (KOH) 3 % and Al powder.

Alternatively, we tested the same reaction without Al, considering that this metal is unsuitable in a successive study under MW irradiation.

Both reactions were carried out with the two different matrices, i.e. siloxane transformer oil (TO) and hydrocarbon engine oil (MO), spiked with Aroclor 1242 (Table 1).

Table 1, near here

The comparison between runs T1 and T2 shows a partially inhibiting role of Al; the total degradation efficiency of PCBs was in fact 54% in the runs without Al, significantly higher than 32% in the runs with Al. On the contrary, Al plays a negligible role in PCB degradation efficiencies, both in the homologic groups and in the total degradation, in the M1 and M2 runs (engine oil).

The comparison of PCB degradation in runs carried out under the same reaction conditions (T1-M1 and T2-M2) highlights a significant matrix effect: the experiments involving TO show higher efficiencies. These results suggest that the different chemical and physical properties of the two oils influence the ability of the systems to create specific interactions between the different mixture compounds, modifying the reactivity of the involved species. In particular, the different dechlorination activity could be ascribed to the different viscosity of the two oil matrices. In fact, the employed siloxane transformer oil is characterized by a viscosity of about 50 $mm^2 s^{-1}$, whereas the hydrocarbon engine one shows an average viscosity of about 100 $mm^2 s^{-1}$. The lower viscosity of siloxane transformer oil can help the mixing and the contact between the reagents, thus favoring the dechlorination reaction, leading to higher % PCB degradations, both in the homologic groups and in the total degradation.

These preliminary experiments give also some insight into the involved reaction mechanisms. According to the literature, the main degradation pathway which occurs should be the nucleophilic substitution dechlorination, although in the presence of Al also the hydrodechlorination mechanism can work.

In our tests, we have not observed accumulation of low chlorine PCBs in the runs working with Al; this suggests that the major mechanism is the nucleophilic substitution, whose reaction pathway is reported in Scheme 1.

Scheme 1, near here

Furthermore, the data of Table 1 suggest that, when TO is employed, Al can fine-tune the mechanism of dechlorination, favoring the reaction from highly chlorinated congeners to less chlorinated ones. In fact, run T1 in the presence of Al shows a higher removal degree for pentachlorinated biphenyls that decrease by 48 % respect to monochlorinated ones, whose reduction was only 12 %. On the contrary, in the absence of Al (run T2, Table 1), the degradation of chlorinated species appears more statistically distributed on an average value of 55-60 % for all congeners.

3.2 Dechlorination activity adopting microwave irradiation

In order to make the PCB removal greener and more sustainable, we tested the employment of MW in the PCB degradation on both oil matrices.

3.2.1 Dechlorination activity adopting MW irradiation on the siloxane transformer oil

The comparison between the employment of traditional heating and MW irradiation on siloxane TO is shown in Figure 1, where the runs T1 and T2 (reaction conditions in Table 1) were carried out adopting traditional heating, whereas T3 was performed under MW irradiation at 100°C and 300 W for 15 minutes in the same reaction conditions (PEG 8000 4.5 % w/w, KOH 3 %).

Figure 1, near here

The use of MW (run T3) gives intermediate PCB degradation efficiency between runs T1 (with Al) and T2 (without Al) adopting a reaction time of 15 minutes under the same reaction conditions. Figure 2A shows that, doubling the reaction time (run T3L, 30 minutes) under the same reaction conditions adopted in run T3 (PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W), the efficiency of PCB degradation is comparable to that of run T2 (reaction time: 2 h).

Figure 2, near here

The comparison between the runs T3 and T3L suggests that the selectivity seems to be addressed towards the degradation of the highly chlorinated congeners, at least with shorter reaction times. From this point of view, MW irradiation works similarly to the metal catalyst. As the reaction proceeds, all the congeners are degraded in the same amount and the reaction has reached an advanced degradation degree.

Employing the simultaneous cooling of the sample (run T3R) with 15 minutes of reaction time, the effect of microwave is maximized, resulting into a total degradation efficiency of 54 %, analogous to that obtained in 2 h adopting traditional heating (run T2). The simultaneous cooling of the reactor with a stream of air on the outside of the reaction vessel allows the heating with a substantial amount of MW energy. It is well-established that the ability of MW to quickly superheat the reactants increases the yield decreasing side reactions. In fact, MW energy is transferred kinetically to the reactants and when higher amount of energy is released to the reactants, greater yields with fewer side reactions were achieved. However, when the power is significantly increased, the risk of overheating temperature-sensitive reactants and of causing degradation of the product can occur. It is possible to solve this problem by cooling the reactor with compressed gas on the outside of the reaction vessel, while simultaneously irradiating the sample with MW energy up to 300 W.

The effect of the molecular weight of polyethyleneglycol on the dechlorination efficiency was investigated. For this purpose, two experiments were performed on TO employing PEG with a lower molecular weight, PEG 200 4.5 % w/w in run T4 and the monomer ethylene glycol (EG) 4.5 % w/w in run T5, both runs carried out under the same reaction conditions (KOH 3 %, 100°C, 15 minutes, 300 W). The reduction of the molecular weight of the reagent causes a significant decrease of the dechlorination activity (Figure 2B), which reaches the lowest value in the presence of EG (run T5). The reason of this trend can be attributed to the different repartition coefficient of PCBs between the oil phase and the glycol: the increase of the molecular weight of PEG can cause an increased solubility of PCB species in the PEG, thus favoring the dechlorinaion reaction. Regarding the selectivity, it is possible to observe that independently from the molecular weight of PEG, the system at the start of the reaction is more active in the dechlorinaion of highly chlorinated congeners which lose one Cl atom at a time, thus increasing the concentration of less chlorinated species until these last ones are in turn activated and dechlorinated. This behavior is markedly evident for run T5 where the concentrations of low-chlorinated biphenyls (mono- and di-chlorobiphenyls) increase compared to their levels in the starting oil. This can be rationalized considering that the activity of the reaction, although low, is aimed at the degradation of high-chlorinated biphenyls (tri-, tetra- and penta-chlorobiphenyls) which give lighter chlorinated species. It is also possible to observe the same behavior in run T4, where the percentages of removal of the first and the second class of congeners were significant lower than those observed for the other more chlorinated classes (tri-, tetra- and penta-chlorobiphenyls).

It is important to highlight that each GC-MS analysis does not evidence the production of polychlorobiphenyl alcohols, precursors of dangerous and toxic polychlorinated dibenzofurans (Choudhary et al., 1983).

To better investigate the role of MW irradiation, three runs were performed on TO employing only MW; this approach has not been reported in the literature so far. Only few blank experiments on real contaminated oils and soils without the addition of any reagents in the only presence of MW are reported in the literature as reference runs (Kamarehie et al., 2014; Tajik et al., 2014; Liu et al. 2008) and evidenced little efficiencies towards PCB removal. The effects of the reaction time, runs T6 performed for 15 minutes and T6L for 30 minutes, and of the simultaneous cooling, run T6R carried out for 15 minutes with cooling, were investigated at 100°C and 300 W and the results are shown in Figure 2C.

The correlation between the increase of the reaction time and the higher dechlorination activity appears clear in siloxane matrix, moving from a total degradation degree of 22 % after 15 minutes up to 26 % after 30 minutes. Moreover, a further improvement in the PCB removal was achieved when the reaction was performed with the simultaneous cooling of the sample, supplying more energy and reaching a total dechlorination value of 32 %. In the literature it has been reported that higher MW power enhances the removal of PCBs (Liu et al., 2008).

The possibility to perform PCB degradation by this MW-assisted process in the liquid phase is quite interesting, because the same does not work under conventional heating conditions. The higher degradation efficiency of MW irradiation respect to conventional heating has been related to the direct interaction of the reaction medium and of the PCB molecules with the MW irradiation, these last being more degraded when the dipole moment is higher. Moreover, the eventual formation of micro/nanoscale hotspots, causing a not uniform temperature of the irradiated medium, can occur (Huang et al., 2011).

3.2.2 Dechlorination activity adopting MW irradiation on the hydrocarbon engine oil

The influence of MW on dechlorination is always positive also for this type of oil in comparison to conventional heating. Figure 3A shows the influence of microwave irradiation time and of cooling system adopting the already tested reaction conditions (PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W), highlighting as run M3 performed under MW irradiation for 15 minutes achieves the same dechlorination efficiencies of run M2 carried out under conventional heating for 2 h.

Figure 3, near here

According to previously described results of experiments with TO, doubling the reaction time under the same reaction conditions (PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W) as evidenced by run M3L, which was carried out for 30 minutes, the total PCB degradation degree increases by 7 %, that is approximately the same amount observed in parallel experiments on TO (run T3 and T3L, Figure 2A).

However, in this case, the effect of the MW combined with simultaneous cooling (run M3R) is not remarkable: runs M3 and M3R after 15 minutes of reaction time under the same reaction conditions show comparable results, as again shown in Figure 3A.

The molecular weight of PEG on dechlorination efficiency evidences the same behavior already observed for the TO matrix, as shown in Figure 3B where run M4 was carried out in the presence of PEG 200, whereas run M5 of ethylene glycol (EG), adopting the same reaction conditions (KOH 3 %, 100°C, 15 minutes, 300 W). Also in the MO system, a progressive reduction in the activity moving from PEG 80000 to PEG 200 and, finally, to EG is ascertained.

The selectivity of PCB degradation in MO seems to follow similar rules as in TO and the concentrations of low-chlorinated biphenyls (mono-, di- and tri-chlorobiphenyls for run M5) increase respect to the initial ones.

Figure 3C shows the results of the experiments carried out in the presence of MW irradiation as the only driving force to explore the effects of reaction time, runs M6 performed for 15 minutes and M6L for 30 minutes, and of the simultaneous cooling, run M6R carried out for 15 minutes with cooling, all runs tested at 100°C and 300 W.

Also in the case of MO oil, GC-MS analysis does not evidence the production of polychlorobiphenyl alcohols.

In this case, the pure MW thermal treatment does not give very encouraging results; the total dechlorination with 15 minutes of reaction time is only 2 % and rises to 7 % by doubling the reaction time. The simultaneous cooling gives poor results too, because the highest efficiency is only 4 %.

3.2.3 Effect of temperature on the dechlorination activity under MW irradiation as the unique driving force on both oil matrices.

In order to investigate the influence of temperature on the dechlorination activity adopting MW irradiation as the only driving force, other two runs, M7 and T8 on MO and TO respectively, have been carried out at 180°C in the presence of the unique MW irradiation. After 15 minutes of reaction, the achieved results are shown in Figure 4 together with the results of the corresponding tests carried out at 100°C (M6 and T7 on MO and TO respectively).

Figure 4, near here

From the figure, it is possible to appreciate an increase of PCB removal efficiencies with temperature for MO oil (compare run M6 with run M7) and a lower increase for the more efficient TO oil (compare run T6 with run T7).

Although in the presence of only MW irradiation the reaction mechanism is not clear and studies are in progress, it is possible to hypothesize that a hydrodechlorination mechanism can occur, as proposed by other authors in the literature for the decomposition of PCBs in the soil (Tanirmchi et al., 1997). To better clarify the degradation pathways, the identification of trace-intermediate products by GC-MS during the process is now in progress testing different reaction conditions.

The comparison of the experiments carried out under MW irradiation on MO confirms that this type of oil is less suitable for PCB degradation, highlighting again a matrix effect. In the presence of MW, this behavior could be rationalized taking into account that the commercial transformer oil based on polydimethylsiloxane has a dielectric constant of 2.8, whereas the engine mineral oil composed of hydrocarbons shows a lower value of the dielectric constant (about 2.0), thus resulting in a slightly lower microwave absorbtion (Farcich N.J. et al., 2008). Moreover the siloxane oil has a water content of 200 ppm which can also slightly contribute to MW absorption by the medium, whereas the engine hydrocarbon oil has the moisture content less than 10 ppm, as determined by Karl Fischer method (ASTM International, 2007).

4. Conclusions

The MW-assisted removal of polychlorinated biphenyls on siloxane transformer oil and hydrocarbon engine oil was studied and compared with traditional heating. The time of MW irradiation, the type and amount of added co-reactants and the temperature result important parameters influencing the dechlorination efficiency. Interesting results in the presence of MW were achieved, reaching up to about 50 % of dechlorination degree, saving time and energy compared to conventional heating. In addition, a remarkable dechlorination degree, up to 32 %, was reached for siloxane transformer oil when MW irradiation was employed in the absence of co-reactants. To the best of our knowledge, this is the first application of the MW irradiation as the unique driving force in a systematic investigation on the dechlorination of heavily polluted siloxane transformer and hydrocarbon engine oils, in the absence of other chemicals. Work is now in progress to improve this MW-approach method, extending the study to other PCB-containing wastes and modifying the reaction conditions, also with the aim of clarifying the involved reaction mechanism.

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Table 1: Influence of Al on the % PCB degradation in homologic groups and % PCB total degradation in the dechlorination of siloxane transformer oil (runs T1 and T2) and hydrocarbon engine oil (runs M1 and M2) compared to the corresponding starting ones, TO (siloxane transformer oil) and MO (hydrocarbon engine oil) added with amounts of Aroclor 1242. The reaction was carried out in the presence of PEG 8000 4.5 % w/w, KOH 3 % for 2 h at 100°C under traditional heating.

Run	**Al w/w**	**Added PCBs (ppb)**					**Total added PCBs (ppb)**
		mono	**di**	**tri**	**tetra**	**penta**	
TO	-	485	9108	37102	28238	6244	81177
MO	-	306	6598	19298	20352	4307	50861
		% PCB Degradation in homologic groups					**% PCB Total Degradation**
T1	0.5 %	12%	32%	33%	29 %	48%	32%
T2	-	65%	57%	51%	55%	62%	54%
M1	0.5 %	27%	24%	15%	20%	20%	19%
M2	-	34%	16%	20%	19%	22%	19%

Highlights

- Microwave irradiation has been applied for the removal of polychlorinated biphenyls.
- Transformer and engine oils were tested for the removal of polychlorinated biphenyls.
- For the first time microwave irradiation was employed as the only driving force.
- Microwave irradiation was used to improve the current industrial removal approach.
- Adopting microwave irradiation promising dechlorination degrees were achieved.

Figure 1 revised

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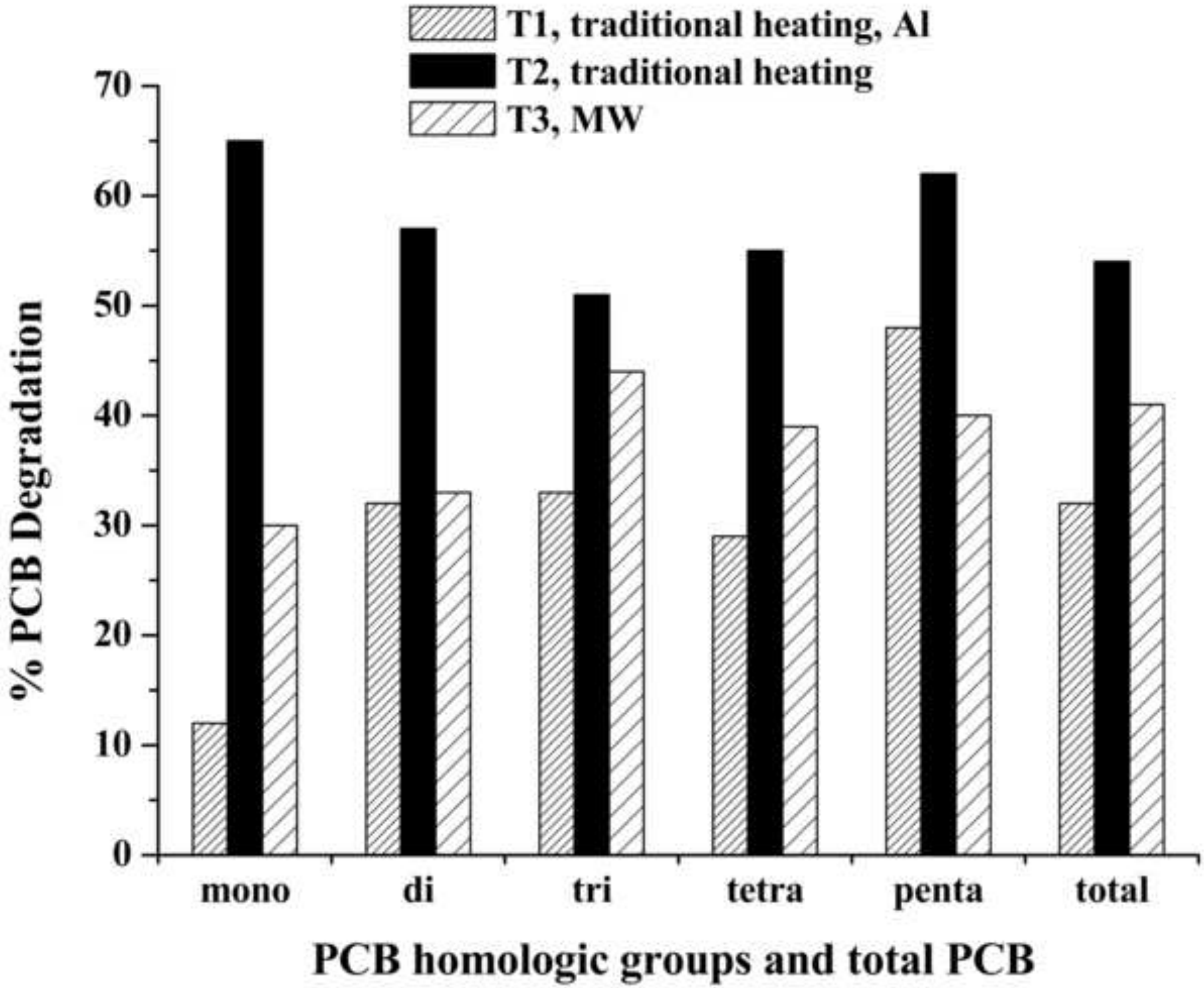
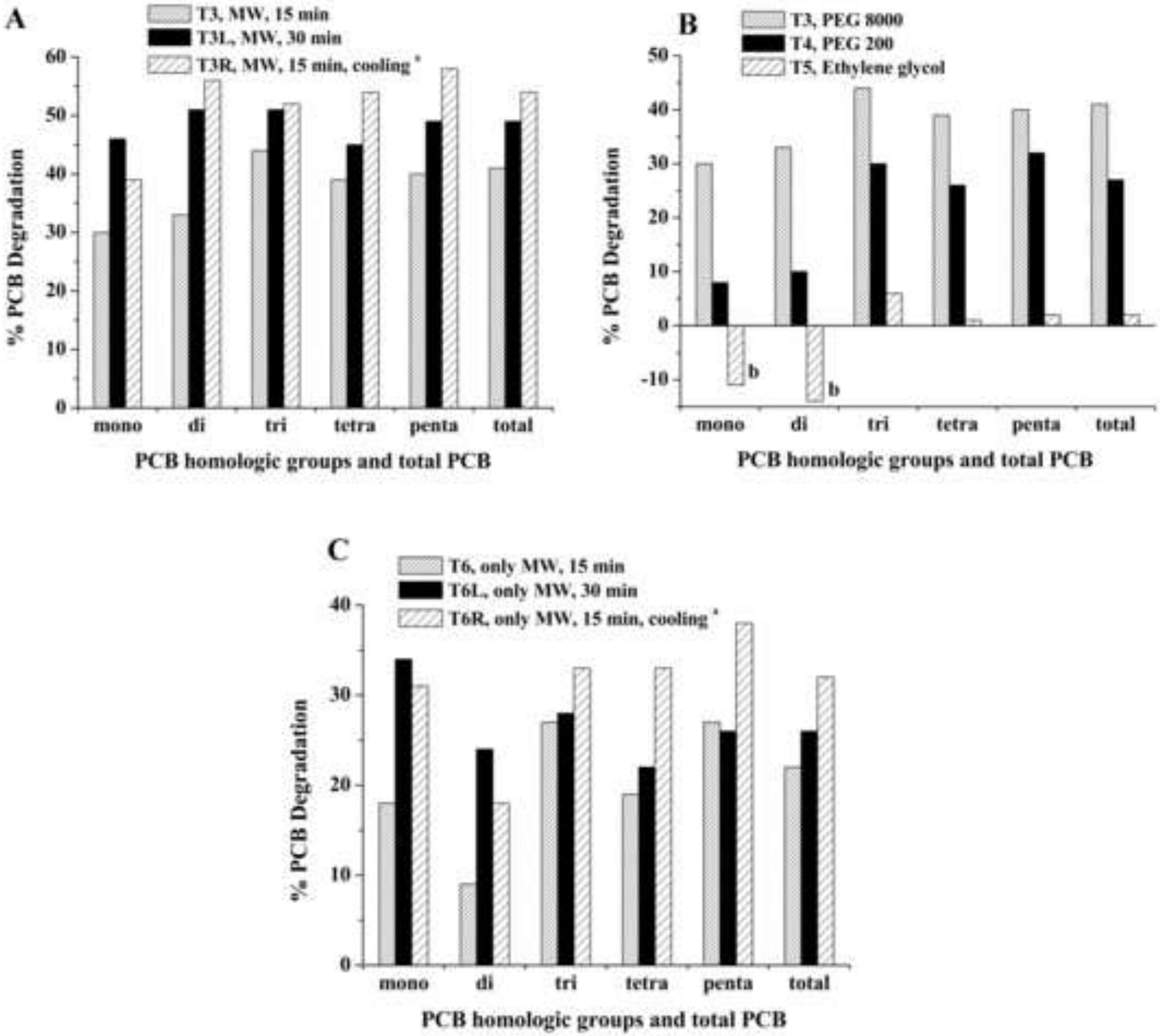


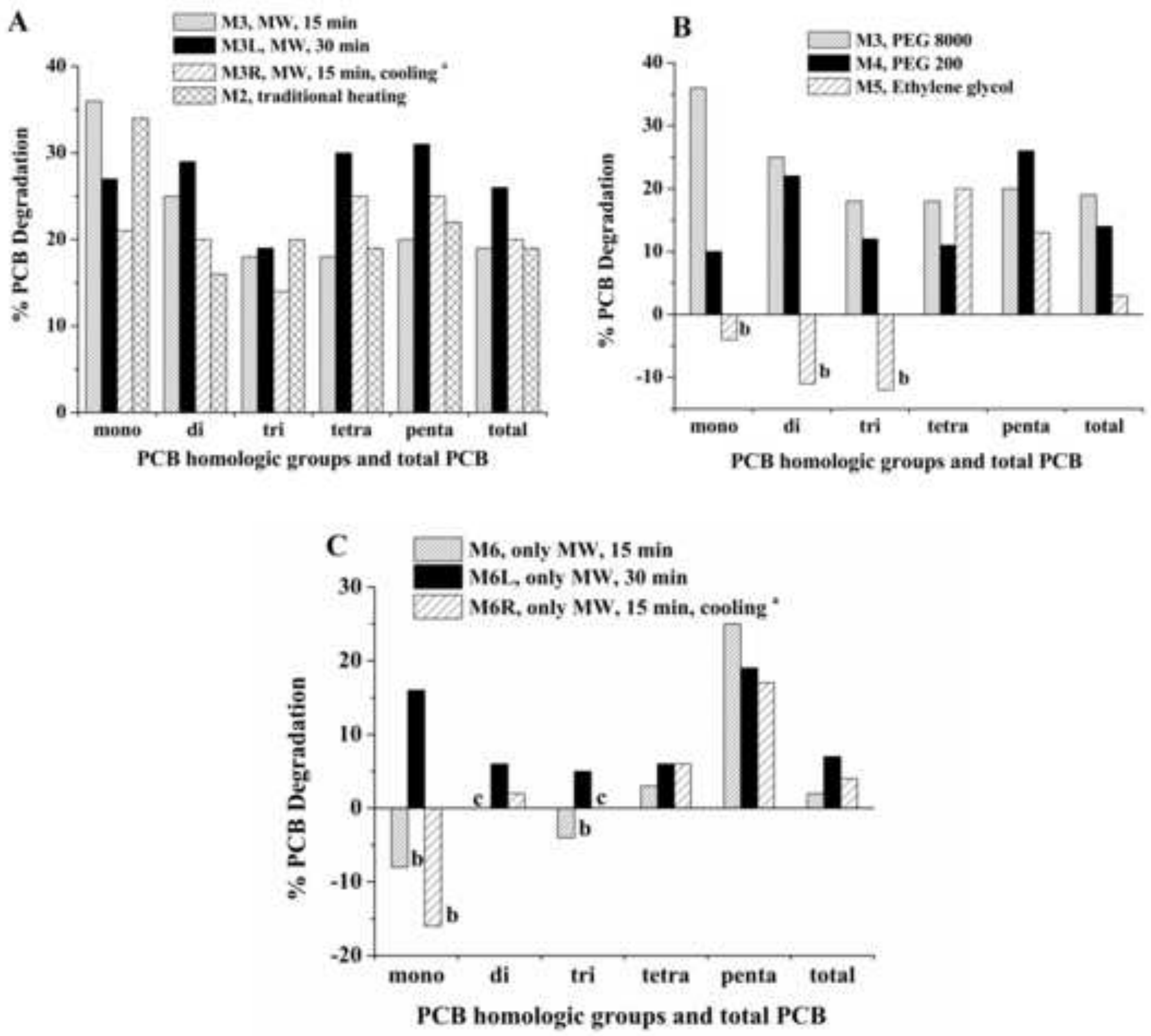
Figure 2 revised



[a] in this case the sample is cooled using air and MW-irradiated at the same time (simultaneous cooling);

[b] negative values mean the increase of the concentrations of the corresponding species.

Figure 3 revised



[a] in this case the sample is cooled using air and MW-irradiated at the same time (simultaneous cooling);
[b] negative values mean the increase of the concentrations of the corresponding species;
[c] this value is zero.

new Figure 4

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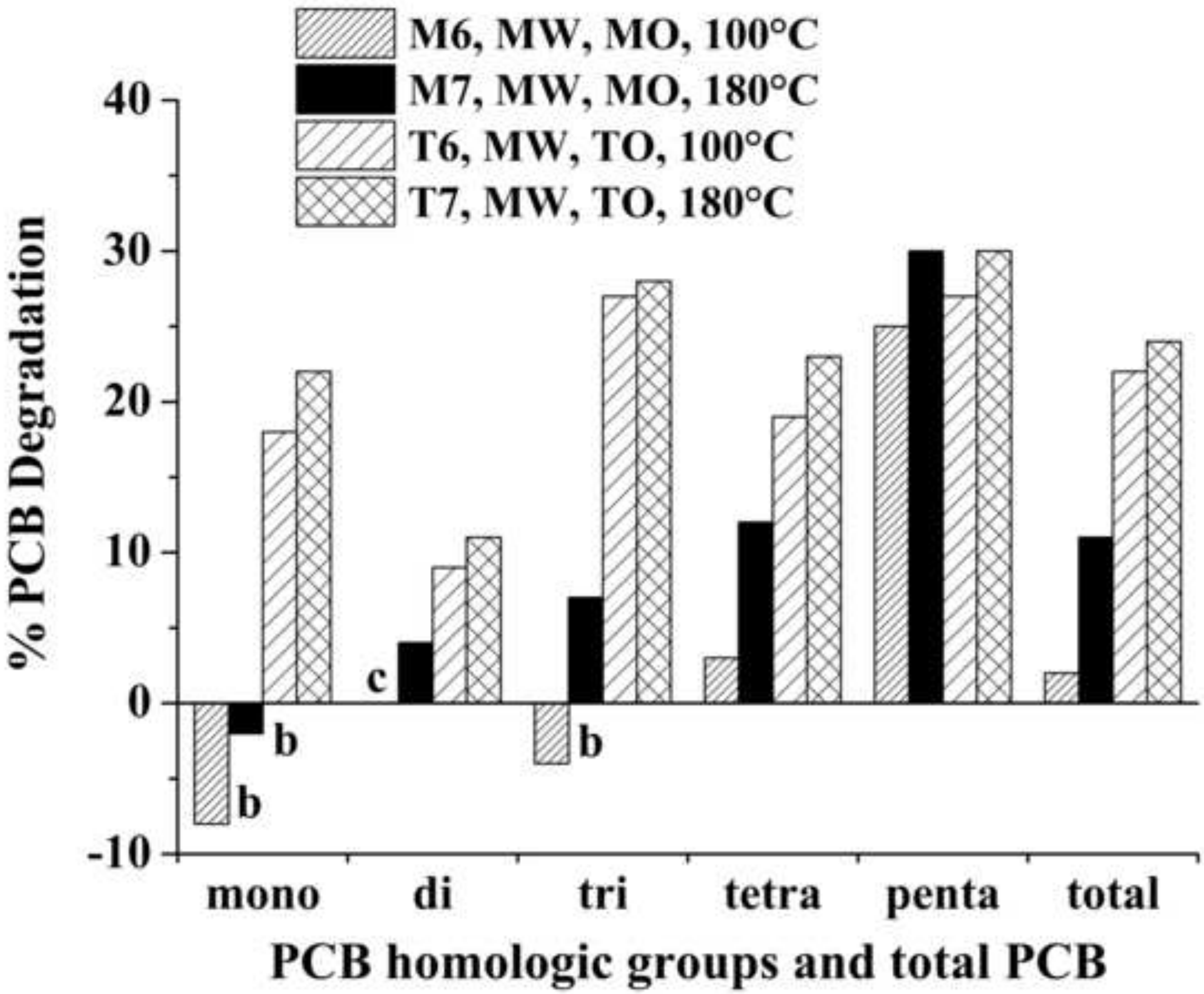
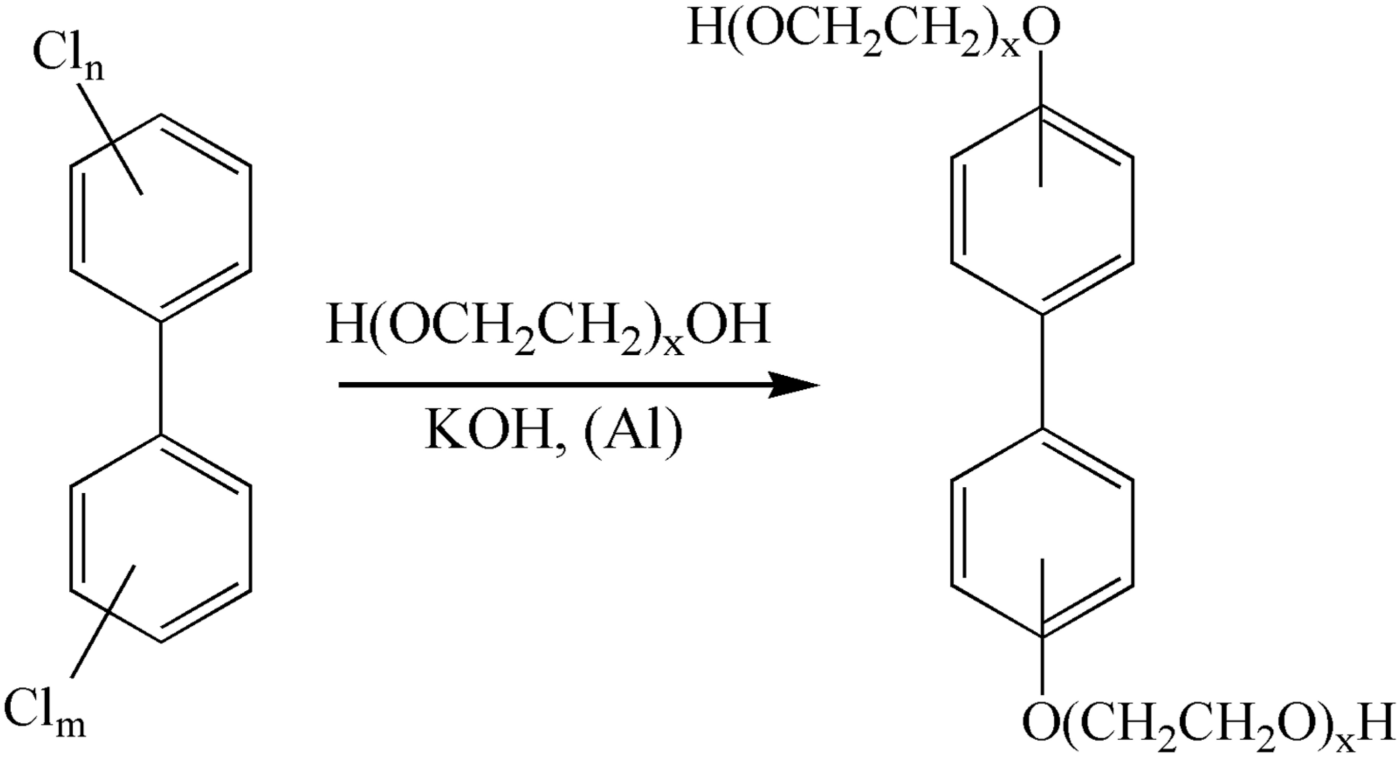


[b] negative values mean the increase of the concentrations of the corresponding species;

[c] this value is zero.

Scheme 1



Captions for Figures

Figure 1: Influence of Al adopting the traditional heating and influence of microwave irradiation compared to traditional heating on the % PCB degradation in homologic groups and % PCB total degradation in the dechlorination reaction of the model transformer oil (reaction conditions: runs T1 and T2, Table 1; run T3, PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W).

Figure 2: % PCB degradation in homologic groups and % PCB total degradation in the dechlorination reaction of the model siloxane transformer oil: A) influence of microwave irradiation time, run T3 15 minutes, run T3L 30 minutes, and of cooling system, run T3R 15 minutes with cooling system, (reaction conditions: PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W); B) influence of the molecular weight of PEG, run T4 PEG 200 4.5 % w/w and run T5 Ethylene glycol 4.5 % w/w, (reaction conditions: KOH 3 %, 100°C, 15 minutes, 300 W); C) influence of microwave irradiation at 100°C and 300 W as the unique driving force, run T6 15 minutes, run T6L 30 minutes and run T6R 15 minutes with cooling.

Figure 3: % PCB degradation in homologic groups and % PCB total degradation in the dechlorination reaction of the model hydrocarbon engine oil: A) influence of microwave irradiation time, run M3 15 minutes, run M3L 30 minutes, and of cooling system, run M3R 15 minutes with cooling system, (reaction conditions: PEG 8000 4.5 % w/w, KOH 3 %, 100°C, 300 W); B) influence of the molecular weight of PEG, run M4 PEG 200 4.5 % w/w and run M5 Ethylene glycol 4.5 % w/w (reaction conditions: KOH 3 %, 100°C, 15 minutes, 300 W); C) influence of microwave irradiation at 100°C and 300 W as the unique driving force, run M6 15 minutes, run M6L 30 minutes and run M6R 15 minutes with cooling.

Figure 4: % PCB degradation in homologic groups and % PCB total degradation in the dechlorination reaction of the model hydrocarbon engine oil and siloxane transformer oil at 100 (run M6 and T6 respectively) and 180°C (M7 and T7 respectively) after 15 minutes employing microwave irradiation as the unique driving force.

Scheme 1: Reaction pathway of the nucleophilic substitution mechanism in the dechlorination of PCBs.

Supplementary Information

S1: Experimental conditions in the dechlorination reaction of the model siloxane transformer oil.

Run	**Time (min)**	**Reagents**		**MW (W)**	**T (°C)**
		glycol	**KOH**		
T3	15	PEG 8000 (4.5 % w/w)	3 %	300	100
T3L	30	PEG 8000 (4.5 % w/w)	3 %	300	100
T3R[a]	15	PEG 8000 (4.5 % w/w)	3 %	300	100
T4	15	PEG 200 (4.5 % w/w)	3 %	300	100
T5	15	Ethylene glycol (4.5 % w/w)	3 %	300	100
T6	15	-	-	300	100
T6L	30	-	-	300	100
T6R[a]	15	-	-	300	100

[a] in this case the sample is cooled using air and MW-irradiated at the same time (simultaneous cooling).

S2: Experimental conditions in the dechlorination reaction of the model hydrocarbon engine oil.

Run	**Time (min)**	**Reagents**		**MW (W)**	**T (°C)**
		glycol	**KOH**		
M3	15	PEG 8000 (4.5 % w/w)	3 %	300	100
M3L	30	PEG 8000 (4.5 % w/w)	3 %	300	100
M3R[a]	15	PEG 8000 (4.5 % w/w)	3 %	300	100
M4	15	PEG 200 (4.5 % w/w)	3 %	300	100
M5	15	Ethylene glycol (4.5 % w/w)	3 %	300	100
M6	15	-	-	300	100
M6L	30	-	-	300	100
M6R[a]	15	-	-	300	100

[a] in this case the sample is cooled using air and MW-irradiated at the same time (simultaneous cooling).

S3: Recovery percentages of the internal standards, PCB 19* and PCB 156*, for each oil sample from the clean-up procedure and the corresponding average value.

Oil Sample	Recovery % PCB 19*	Recovery % PCB 156*	Average Recovery %
TO	104	95	99
T1	67	75	71
T2	98	101	100
T3	77	90	83
T3R	99	75	87
T3L	74	91	83
T4	61	65	63
T5	65	80	72
T6	40	58	49
T6R	85	95	90
T6L	85	80	83
MO	36	73	55
M1	38	67	52
M2	93	86	90
M3	58	85	72
M3R	50	76	63
M3L	51	77	64
M4	74	90	82
M5	62	85	73
M6	53	89	71
M6R	30	66	48
M6L	34	79	57