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

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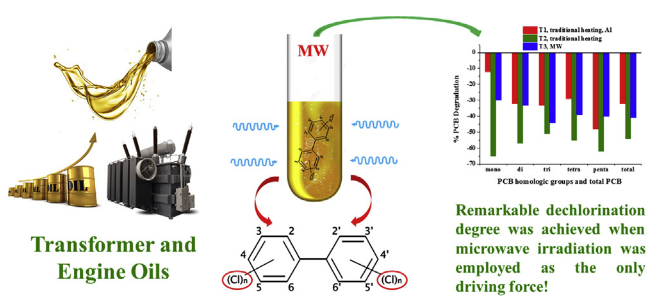
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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.

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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., 2008; Wang et al., 2016; Wu et al., 2005, 2012; 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., 2008, 2011; 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 min 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 min 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 min (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