THESIS ON CHEMISTRY AND CHEMICAL ENGINEERING G37

Peroxygen Compounds and New Integrated Processes for Chlorinated Hydrocarbons Degradation in Contaminated Soil

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Marika Viisimaa

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Peroksü-ühendite ja uute integreeritud protsesside kasutamine kloorsüsivesinike lagundamiseks saastatud pinnases

MARIKA VIISIMAA

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LIST OF PUBLICATIONS

The present doctoral thesis is based on the following original publications referred to by Roman numerals I-V in the text:

I. Goi, A., **Viisimaa, M.**, Trapido, M., Munter, R. (2011). Polychlorinated biphenyls-containing electrical insulating oil contaminated soil treatment with calcium and magnesium peroxides. – *Chemosphere*, 82, 1196-1201.

II. **Viisimaa, M.,** Veressinina, J., Goi, A. (2012). Treatment of Aroclor 1016 contaminated soil by hydrogen peroxide: laboratory column study. – *Environmental Technology*, 33(17), 2041-2048.

III. Goi, A., **Viisimaa, M.**, Karpenko, O. (2012). DDT-contaminated soil treatment with persulfate and hydrogen peroxide utilizing different activation aids and the chemicals combination with biosurfactant. – *Journal of Advanced Oxidation Technologies*, 15(1), 41-52.

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V. **Viisimaa, M.**, Goi, A. (2014). Use of hydrogen peroxide and percarbonate to treat chlorinated aromatic hydrocarbon-contaminated soil. – *Journal of Environmental Engineering and Landscape Management,* 22(1), 30-39.

Other publications related to the research:

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Viisimaa, M., Bolobajev, J., Goi, A. (2013). Ozonation and ultrasound-assisted advanced oxidation processes for degradation of polychlorinated biphenyls in soil. – Proceedings of the Ozone and Related Oxidants in: Safe Water along its Cycle: International Conference EA3G2013, in the framework of Wasser Berlin International Trade Fair and Congress. Berlin, Germany, 23-24 April, 2013, 3.1-1-3.1-7.

Goi, A., **Viisimaa, M.** (2012). Chemical oxidation of chlorinated hydrocarbons in soil utilising peroxygen chemicals, different activation aids and biosurfactants. – Proceedings of the International Conference - Exhibition on Soils, Sediments and Water: Intersol'2012, Word Event Business Solutions - WEBS. Paris-Sud, France, 27-30 March 2012.

Viisimaa, M., Veressinina, J., Goi, A. (2011). Enhanced degradation of polychlorinated biphenyls in soil by hydrogen peroxide, persulfate and ozone. – Proceedings of the Ozone and UV Leading-Edge Science and Technologies: 20th IOA World Congress - 6th IUVA World Congress, Paris, France, 23-27 May. (Eds.) The International Ozone Association and the International Ultraviolet Association, 2011, 1.5.10-1-1.5.10-10.

Goi, A., **Viisimaa, M.**, Trapido, M. (2011). Peroxidation for remediation of chlorinated hydrocarbons contaminated soil. – Proceedings of the FCES' 2011, Finnish Conference of Environmental Science, Turku, Finland, 5-6 May, 2011. (Eds.) Brozinski, J.-M.; Brozonski, A.; Kronberg, L. Åbo Akademi University Printing Press, 29-32.

Goi, A., **Viisimaa, M.**, Trapido, M., Munter, R. (2010). Aroclor 1016 contaminated soil remediation with calcium and magnesium peroxides. – E-Proceedings of the Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA, May 24-27, 2010. (Eds.) Battelle Press.

AUTHOR'S CONTRIBUTIONS TO THE PUBLICATIONS

The contribution of the author to the papers listed below is as follows:

I. The author participated in the writing of the paper. She performed the experimental work and interpreted the results.

II. The author wrote the paper and is the corresponding author. She carried out the experimental work and interpreted the results.

III. The author participated in the writing of the paper. She carried out the experimental work and interpreted the results.

IV. The author wrote the paper and is the corresponding author. She supervised the experimental work of M.Sc. student and interpreted the results.

V. The author participated in the writing of the paper, carried out the main part of the experimental work, and interpreted the results.

INTRODUCTION

Soil contamination is driven by insufficient agriculture, construction works, industrial actions, etc. It was evaluated that approximately three million sites in the European Union is contaminated. Half million sites are extremely contaminated and in need of treatment (EC, 2010). Therefore, the European Commission adopted a EU strategy (EC, 2010) dedicated to soil protection in September 2006. One of the main strategy goals was the contaminated soils remediation to a level that was at least consistent with present and future use. Organochlorine pesticides, such as lindane and dichlorodiphenyltrichloroethane, industrial chemicals, such as polychlorinated biphenyls, chlorinated solvents, and waste products, such as dioxins and furans, among others, are examples of chlorinated hydrocarbons. In spite of the decrease in the production and use of some priority chlorinated compounds over recent decades due to bans and other restrictions, they remain widespread.

Chemical oxidation is a promising treatment method for degrading a variety of hazardous pollutants in different environmental matrixes. Although chemical oxidation has been successfully applied in water purification, its application for soil treatment has been hampered by the lack of scientific knowledge of the process controlling parameters. Hydrogen peroxide is one of the most extensively used chemicals for contaminated soil remediation. The study of emerging oxidation processes using peroxygen chemicals, such as persulphate, calcium peroxide, magnesium peroxide and percarbonate for contaminated soil remediation is the most innovative direction in this area, providing technologically feasible, economically acceptable and environmentally sufficient techniques. In addition to the chemical oxidation of contaminants, utilisation of optimised chemical dosages can potentially enhance aerobic biodegradation of contaminants in soil. A well-executed chemical-to-biological treatment approach or their combined application can result in considerable contaminant reduction and may yield substantial cost savings.

Along with the other methods, the application of surfactants has been demonstrated to be effective as a standalone treatment (Svab et al., 2009), as well as in combination with other methods (Rahman et al., 2003). Surfactants improve solubilisation and desorption behaviour of hydrophobic organic compounds and simultaneously increase their availability (or bioavailability) in contaminated environments (Kuyukina et al., 2005). Biosurfactants may substitute their synthetic counterparts in environmental applications due to their biodegradability, low toxicity and high efficiency under various conditions. It was also reported that biosurfactants may enhance biodegradation through enzyme stimulation (Wang et al., 2011) or promote better permeability of the cellular membranes of hydrocarbon-degrading microorganisms (Vasileva-Tonkova et al., 2011). However, this technique has to be integrated in a more complex process to degrade contaminants, rather than transferring them to a separate medium. Another promising approach could be the application of microbial surfactants (biosurfactants) to integrated chemical and biological oxidation processes, where they may act as oxidation stimulators by releasing contaminants adsorbed in soil into the liquid medium and thus increasing their availability to the oxidising agents and microorganisms.

Among the aims of the present study was to establish effective treatment methods using peroxygen chemicals (persulphate, percarbonate, calcium and magnesium peroxides) for the remediation of soil contaminated with chlorinated hydrocarbons and to develop a new strategy of process integration by the joint application of biosurfactant and combined chemical and biological treatment for soil decontamination. The research should provide the scientific basis and recommendations for the practical application of efficient, simple and cost-effective treatment methods for the remediation of contaminated soil.

ABBREVIATIONS

BS	Biosurfactant
CB	Chlorobenzenes
CCr	Chlorocresols
CHC	Chlorinated hydrocarbons
CMC	Critical micelle concentration
CTh	Chlorothymols
DDT	1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane
DDD	2,2-bis(4-chlorophenyl)-1,1-dichloroethane
DDE	2,2-bis(4-chlorophenyl)-1,1-dichloroethylene
DHA	Dehydrogenase activity
EDTA	Ethylenediaminetetraacetic acid
MO	Microorganisms
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
UV	Ultraviolet

1. LITERATURE REVIEW

1.1 Soil contamination

Soil is a mixture of minerals and organic matter that is produced by the weathering action of physical, chemical and biological processes. High populations of bacteria, fungi and animals may be found in the soil (Manahan, 2004). Soil that has received large quantities of waste products loses its natural texture and quality. This phenomenon can affect human beings health and quality of food. It has been estimated that 3.5 million sites alone in the EU may be contaminated. There are approximately 300 contaminated sites in Estonia (EC, 2010).

1.1.1 Chlorinated hydrocarbons

Chlorinated hydrocarbons (CHC) are chemical compounds, where at least one hydrogen atom has been replaced by chlorine atom. CHC are mostly thermally and chemically stable. These compounds are toxic and persistent in the environment. Soils that are contaminated with CHC make up approximately 2.4% of all of the pollutants (EPA, 2011).

Polychlorinated biphenyls (PCB) belong to a group of organic compounds that consist of two benzene rings and one to ten chlorine atoms (O'Neil, 1996). The physical-chemical properties of PCB vary greatly, depending on the number of chlorine atoms in the molecule (Fiedler, 2009). PCB were used in heat exchange fluids (electric transformers and capacitors) and as additives in paper, paints, adhesives, sealants and plastics. In the 1970s, the production of PCB was banned, but they still persist in the environment. PCB enter the environment during its manufacture, storage, disposal and utilisation processes (Toxic substances, 2013). The good solubility of PCB in the adipose tissue of wildlife and human beings causes bioaccumulation (WHO, 1976).

Dichlorodiphenyltrichloroethane (DDT) is most notable organochlorine pesticide. The DDT commercial product contains 70 to 80% of the insecticidal isomer DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) (Walker, 2001). DDD (2,2-bis(4-chlorophenyl)-1,1-dichloroethane) and DDE (2,2-bis(4-chlorophenyl)-1,1-dichloroethylene) are the by-products of DDT degradation. DDT was primarily used for vector control of diseases (malaria), ectoparasites of farm animals, for agricultural pests and in domestic and industrial premises (Walker, 2001; Toxic substances, 2013). In 1970, the use of DDT was prohibited in the United States. Some other countries soon adopted similar restrictions on DDT use. DDT is very persistent and can accumulate in food chains (EPA 1990; Toxic substances, 2013).

Chlorobenzenes (CB) are chlorinated derivatives of benzene that have at least one chlorine atom. The physical-chemical properties of CB are dependent on the number of chlorine atoms and the position of the chlorine atoms on the benzene ring. CB are mainly used as industrial solvents, as constitutes of pharmaceutical products and pesticides (Daintith, 2008). Chlorocresols (CCr) and chlorothymols (CTh) are chlorinated phenols that have been used as effective antiseptics and preservatives. CBs, CCr and CTh are released to the environment during manufacturing or product spillages.

1.2 Soil treatment

The principal methods of soil treatment are physical/chemical, thermal and biological (Fox, 1996). If the contaminated sites are not highly contaminated, it is possible to use bioremediation only. It is a treatment method that involves stimulating the microorganisms to grow by using the contaminants as a food and energy source. The combination of chemical and biological methods is a complex approach that may be necessary for the remediation of heavily contaminated soil. Chemical oxidation is among the perspective chemical treatment methods applied for the degradation of various hazardous substances in soil.

1.2.1 Chemical oxidation

To degrade a variety of hazardous compounds of soil at waste disposal and spill sites, chemical oxidation is a promising treatment method. Hydrogen peroxide is one of the most extensively used chemicals for contaminated soil remediation. Emerging oxidation processes with the use of peroxygen chemicals, such as, persulphate, calcium peroxide, magnesium peroxide and percarbonate, for contaminated soil remediation are the most innovative techniques in this area.

1.2.1.1 The hydrogen peroxide treatment

Hydrogen peroxide is the most widely used chemical for soil treatment. Hydrogen peroxide is generally applied with Fe(II), giving the classic Fenton reaction [Eq. 1] (Walling, 1975).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad [1]$$

The hydroxyl radical (${}^{\bullet}OH$) formed in the reaction [Eq. 1] can non-selectively react with the C-H bounds of organic molecules and is capable of degrading many pollutants. The reactions [Eqs. 2-4] occur until the hydrogen peroxide is fully consumed (Huling and Pivetz, 2006).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad [2]$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \qquad [3]$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad [4]$$

Decomposition of H_2O_2 can release O_2 that may stimulate aerobic microbial activity (Yin and Allen, 1999).

Hydrogen peroxide oxidation is usually activated by ferrous iron. However, most ions of transition metals (Cu^{2+}, Co^{2+}, Cr^{2+}, Mn^{2+}, Zn^{2+}, etc.) and their minerals presented in soil can also decompose hydrogen peroxide (Watts et al., 1990; Miller and Valentine, 1999; Huling and Pivetz, 2006). Surface reactions that could proceed during the soil treatment (Miller and Valentine, 1999) are the following:

$S^+ + H_2O_2 \rightarrow S + H^+ + HO_2^{\bullet}$ [5]

$S + H_2O_2 \rightarrow S^+ + {}^{\bullet}OH + HO^-$ [6]

$S^+ + O_2^- \rightarrow S + O_2$ [7]

$S + HO_2^{\bullet} \rightarrow S^+ + HO_2^-$ [8]

$S + {}^{\bullet}OH \rightarrow S^+ + HO^-$ [9]

where S is the reduced metal oxide-coated sand surface site, and S^+ is the oxidised metal oxide-coated sand surface site. Hydrogen peroxide can react with oxidised and reduced surface sites [Eqs. 10-12].

$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$ [10]

$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet -}$ [11]

$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^- + O_2$ [12]

Superoxide anions ($O_2^{\bullet -}$), hydroperoxide anions (HO_2^-) and perhydroxyl radical ($HO_2^{\bullet}$) can act as the reductant/oxidiser, initiating oxidation reactions in the liquid phase during the soil treatment process. These species may occur when the concentration of hydrogen peroxide is high ($\geq 2\%$) in the soil (Watts et al., 1990).

Hydrogen peroxide can oxidise a wide range of contaminants in soil, such as fuel hydrocarbons (Watts and Dilly, 1996; Kong et al., 1998; Goi et al., 2006a,b), polycyclic aromatic hydrocarbons (PAH) (Kulik et al., 2006; Palmroth et al., 2006a,b), nitrophenols (Goi and Trapido, 2004), chlorinated solvents (Teel et al., 2001; Vicente et al., 2011), volatile organic compounds (Gates-Anderson, 2001), etc.

1.2.1.2 The calcium and magnesium peroxide treatment

Calcium and magnesium peroxides are both used for the chemical oxidation of contaminants and to enhance aerobic bioremediation. Calcium or magnesium peroxide decomposes slowly in contact with water, releasing heat and oxygen over an extended time period [Eqs. 13, 14]. Raised oxygen content in the subsurface layer can increase aerobic biodegradation (Cassidy and Irvine, 1999; Kao et al., 2001).

$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2$ [13]

$2MgO_2 + 2H_2O \rightarrow 2Mg(OH)_2 + O_2$ [14]

This process can exist for periods of up to one year, depending on site conditions, such as soil pH, the amount of organics and metals, contaminant type, concentrations, etc.

If the pH of the soil is high ($pH \geq 12$), hydrogen peroxide is usually not generated, but at lower pH values, hydrogen peroxide is produced [Eqs. 15, 16] (Nortup and Cassidy, 2008). Hydrogen peroxide can react through the direct oxidation of the contaminant or through the formation [Eqs. 1-4] of hydroxyl radicals and the other oxidative/reductive species.

$2CaO_2 + 2H^+ \rightarrow 2Ca^{2+} + H_2O_2$ [15]

$2MgO_2 + 2H^+ \rightarrow 2Mg^{2+} + H_2O_2$ [16]

The utilisation of calcium and magnesium peroxides can avoid the disadvantages of liquid hydrogen peroxide use, such as violent exothermic reactions, the need for pH control and rapid oxidant consumption.

Calcium peroxide has been mostly known and applied as the stimulator of aerobic bioremediation of contaminants in soil (Cassidy and Irvine, 1999) and groundwater (Kao et al., 2001, 2003; Liu et al., 2006). There are only couple of studies where calcium peroxide was applied as the source of hydrogen peroxide for chemical oxidation of contaminants in soil (Northup and Cassidy, 2008) and water (Arienzo, 2000).

1.2.1.3 The persulphate treatment

Persulphate occurs in the form of sodium, potassium and ammonium salts. Sodium persulphate is the most common and feasible form of the oxidative chemical used in soil treatment (Block et al., 2004; Huling and Pivetz, 2006; Tsitonaki et al., 2010).

Sodium persulphate dissociates in water to persulphate anions [Eqs. 17, 18].

$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{2-}$ [17]

$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$ [18]

The persulphate anion ($S_2O_8^{2-}$) is the most powerful oxidant in the peroxygen family (Block, 2004; Huling and Pivetz, 2006).

Persulphate can generate a free radicals pathway through the formation of sulphate radicals, if it is activated by heat, transition metals or UV-radiation [Eqs. 19-22] (Huling and Pivetz, 2006; Tsitonaki et al., 2010).

$S_2O_8^{2-} + \text{initiator} \rightarrow SO_4^{\bullet-} + (SO_4^{\bullet-} \text{ or } SO_4^{2-})$ [19]

Heat and UV activation:

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ [20]

Transition metals activation:

$S_2O_8^{2-} + M^{n+} \rightarrow M^{n+1} + SO_4^{2-} + SO_4^{\bullet-}$ [21]

$SO_4^{\bullet-} + M^{n+} \rightarrow M^{n+1} + SO_4^{2-}$ [22]

Heat and ferrous iron activation of persulphate are effective at the bench scale, but in field application, it has some limitations and disadvantages (Huling and Pivetz, 2006). Heat activation requires the installation of a parallel heating system to heat the entire contaminated field, which is expensive. Fe(II) activation is limited in field applications by its transportability. Iron (II) is oxidised by the persulphate to iron (III), which is insoluble at pH > 4 [Eqs. 23-25] (Block, 2004; Dahmani et al., 2006). Even through that, ferrous iron is the most commonly used transition metal as an activator. It is generally applied in the form of ferrous sulphate and chloride. The amount of iron should be kept in mind because excessive ferrous iron may result in the rapid decomposition of persulphate and consequently, a loss in oxidation performance (Block et al., 2004).

$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+}$ [23]

$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$ [24]

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$ [25]

Sulfate radicals are reactive species, which have a short lifespan and can oxidise various organic compounds. Following sulphate radical generation, a series of reactions can proceed, involving the formation of other active species [Eqs. 26-28] (Tsitonaki et al., 2010).

$SO_4^{\bullet-} + OH^- \rightarrow {}^{\bullet}OH + SO_4^{2-}$ [26]

$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+$ [27]

$2^{\bullet}OH \rightarrow H_2O_2$ [28]

There are several studies where persulphate was effectively used for the degradation of PAH (Teel et al., 2009), diesel fuel (Liang and Guo, 2012), chlorinated solvents (Liang et al., 2004, 2008; Dahmani et al., 2006), dinitrotoluene (Cassidy et al., 2009), etc.

1.2.1.4 The percarbonate treatment

Percarbonate is a solid carrier of hydrogen peroxide. This chemical compound is also named as carbonate perhydrate. Sodium percarbonate is not persistent in the environment; it decomposes readily in the presence of water to sodium carbonate and hydrogen peroxide [Eq. 29], and the latter will subsequently decompose to water and oxygen [Eq. 30] (McKillop and Sanderson, 1995; Rivas et al., 2010). Oxygen formation in the subsurface layer supports the aerobic biodegradation of the contaminant.

$2Na_2CO_3 \bullet 3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2$ [29]

$2H_2O_2 \rightarrow 2H_2O + O_2$ [30]

Sodium percarbonate dissolves in water to sodium carbonate and hydrogen peroxide, creating an alkaline oxidative environment. Because pH is alkaline, nucleophilic perhydroxyl ion is formed from hydrogen peroxide [Eq. 31] (McKillop and Sanderson, 1995).

$H_2O_2 \rightarrow H^+ + HO_2^-$ [31]

The potential disadvantage of sodium percarbonate could be the scavenging of the hydroxyl radical exerted from the release of bicarbonate anions [Eqs. 32-34].

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$ [32]

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ [33]

$HCO_3^- + {}^\bullet OH \rightarrow HCO_3^\bullet + OH^-$ [34]

However, the carbonate radical anions ($CO_3^{-\bullet}$) generated by the reactions [Eqs. 35, 36] were reported to yield a reduction potential ($CO_3^{-\bullet}$, H^+/HCO_3^-) of 1.63 V at pH 8.4 and found to be effective for the degradation of various aromatic compounds, such as benzene, p-xylene, toluene, chlorobenzene, nitrobenzene and benzonitrile (Zuo et al., 1999; Umschlag and Hermann, 1999).

$HCO_3^\bullet \leftrightarrow H^+ + CO_3^{-\bullet}$ [35]

$CO_3^{2-} + {}^\bullet OH \rightarrow CO_3^{-\bullet} + OH^-$ [36]

Bicarbonate anions can also react with hydrogen peroxide to generate peroxymonocarbonate ions (HCO_4^-) [Eq. 37] and several other active oxygen species, such as superoxide ions (O_2^-) and singlet oxygen (${}^1O_2$) (Flangan et al., 1986).

$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O$ [37]

Bicarbonate anions have a negative effect on treatment efficacy, but carbonate radical anions promote effective degradation of various contaminants (Glaze et al., 1995; Ku et al., 1996).

A bicarbonate-activated hydrogen peroxide system has been found to be capable of oxidising a variety of organic compounds in the liquid phase. Moreover, the reactivity of peroxymonocarbonate ions towards organic sulphides has been found to be higher than that of hydrogen peroxide by a factor of 100 to 500, depending on the specific substrates. Thus, the chemistry of the percarbonate oxidation system is more complicated than previously suggested and may allow for the destruction of a wide range of resistant contaminants in soil and water (Flangan et al., 1986; Yao and Richardson, 2000; Regino and Richardson, 2007).

There are three published studies (Cravotto et al., 2007; Bumbac and Diacu, 2012; De La Calle et al., 2012) on the application of percarbonate for contaminated soil treatment. Cravotto et al. (2007) combined sodium percarbonate with microwaves and the complete degradation of aromatic compounds (4-chloronaphtol, 2,4-dichlorophenoxyacetic acid) in soil was achieved. Bumbac and Diacu (2012) combined sodium percarbonate with biological treatment (natural attenuation) for diesel contaminated soil. De La Calle et al. (2012) evaluated the effect of the addition of sodium percarbonate solution to PAH contaminated soil. There are no significant studies on the comparison of the efficacy of the contaminated soil treatment methods that utilised a solid hydrogen peroxide carrier (percarbonate) and the liquid one (hydrogen peroxide).

1.2.2 Biosurfactant in the soil treatment

Surfactants improve the solubilisation and desorption behaviour of hydrophobic organic compounds and increase their availability in contaminated environments (Kuyukina et al., 2005). Biosurfactant application for soil remediation is a promising technology due to its biodegradability, biocompatibility and low toxicity (Mulligan, 2005). Biosurfactants are biologically produced by yeast or bacteria from various substrates, such as oils, waste, alkanes, sugars, etc. (Lin, 1996). They can be industrially produced from cheap raw materials, which are available in large amounts (Noordman et al., 1998; Mulligan, 2005). Biosurfactants may enhance biodegradation through enzyme stimulation or promote better permeability of cellular membranes of hydrocarbon-degrading microorganisms (Wang et al., 2011; Vasileva-Tonkova et al., 2011). Surfactants permit to bring a molecule to the surface and could decrease surface tension. Surface tension, interfacial tension and solubilisation are presented in *Figure 1* as a function of surfactant concentration. Efficient surfactants have a low critical micelle concentration, which means that less surfactant is required to decrease the surface tension (Mulligan, 2005).

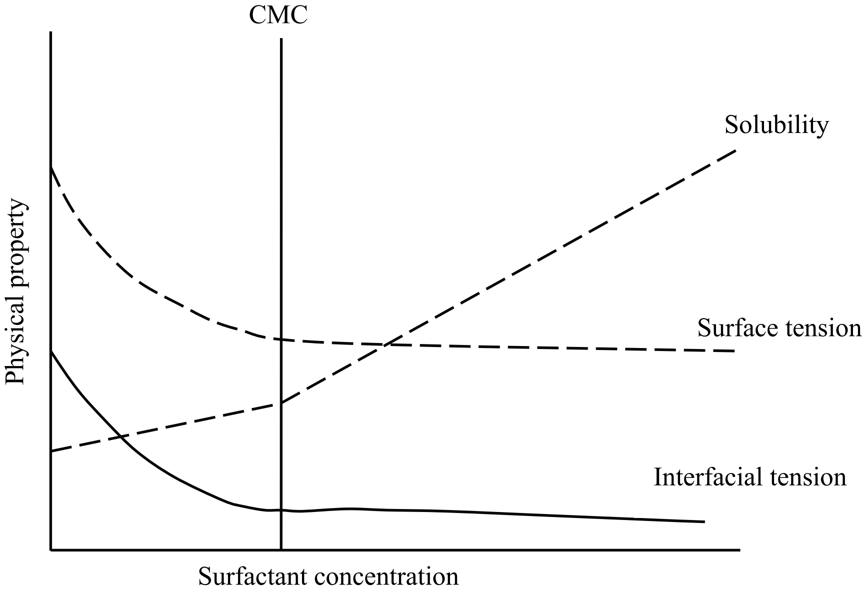

Figure 1. Surface tension, interfacial tension and solubilisation as a function of surfactant concentration (Mulligan, 2005).

Biosurfactants can be integrated into the chemical and biological oxidation processes. Biosurfactants can act as oxidation stimulators by releasing contaminants adsorbed in the soil into the liquid medium and thus, increasing their availability to oxidising agents and microorganisms.

Complex approaches involving combined chemical and biological methods, along with the addition of biosurfactants may be necessary for the remediation of heavily contaminated soil. However, the effect of the joint application of biosurfactants and combined chemical–biological treatment remains unknown due to the lack of appropriate studies. In addition, the influence of the simultaneous application of biosurfactants and either natural microbial consortia isolated from contaminated media or chemical oxidants on PCBs degradation has not been reported.

1.3 The aims of the study

The objectives of the present research were as follows:

- to test the treatment methods using new peroxygen chemicals (persulphate, percarbonate, calcium and magnesium peroxides) for the remediation of chlorinated hydrocarbons contaminated soil;
- to test different activation aids (supplemental application of non-chelated/chelated ferrous and ferric iron, chelation of natural transition metals of soil, base activation of persulphate, combined application of persulphate and hydrogen peroxide, application of acidic pH conditions to sustain the persulphate and hydrogen peroxide activation processes);
- to optimise treatment conditions (dosages, treatment time and treatment mode) to achieve the maximum reduction efficacy of CHC and minimise stress on soil bacteria after the application of strong oxidants of the peroxygen family to support subsequent biodegradation of the contaminants in soil by indigenous microorganisms;
- to develop a new strategy of process integration through the joint application of biosurfactants and combined chemical and/or biological treatment (using a natural consortium of microorganisms-hydrocarbons destructors) for soil decontamination.

2. MATERIALS AND METHODS

2.1 Soil characteristics and the preparation

Natural topsoil (0-20 cm) was dried overnight at 30ºC in a circulating air drying oven and sieved through < 3.0 mm sieves before the spiking (*Paper I-V*). Several characteristics of the soils are presented in *Table 1*.

Table 1. Several properties of soils

Parameter, unit	Sandy silt soil	Sandy soil
pH	5.2-7.3	5.7
Ferrous iron, g/kg of soil	1.9±0.5	0
Total extractable iron, g/kg of soil	12.1±0.9	11±1.5
Ion-exchangeable Fe(II) fraction, mg/kg of soil	2.0±0.3	0
Organic carbon, mg/kg of soil	460±30	44±4
Sand, %	45.5	99.5
Silt, %	52	0.5
Clay, %	2.5	0

The texture of the soil was identified as sandy silt (*Paper I-V*) and sandy soil (*Paper II*).

2.2 Soil contaminants

Soil samples were artificially contaminated with PCB-containing oil (*Paper I, II, IV*), a commercial DDT mixture (*Paper III*) and a mixture of chlorinated aromatic hydrocarbons, such as p-DCB, p-C-m-Cr and p-CTh (*Paper V*). The methodology of soil preparation and contamination was described in the *Experimental Methods* section of *Papers I-V*. Contaminants concentrations in the soil are given in *Table 2*.

Table 2. Contaminants concentrations in the soil

Contaminant	Concentration, g/kg of dry soil	Paper
Aroclor 1016	39±1	I
Aroclor 1016 (in sandy silt soil)	45.2±0.2	II
Aroclor 1016 (in sandy soil)	52.1±1.6	II
DDT	1.16±0.21	III
DDD	0.42±0.10	III
DDE	0.14±0.06	III
Clophen A30	52±1	IV
p-DCB	0.77±0.03	V
p-C-m-Cr	0.59±0.06	V
p-CTh	2.50 ±0.14	V

2.3 Soil treatment

Soil treatment was carried out in three different ways: in slurry under batch condition (*Paper I, II, III, V)*, in a 60%-watered soil (*Paper I, III, IV),* and in columns (*Paper II)*.

Contaminated soil in the slurry was treated for 24 h in a cylindrical glass reactor with a volume of 0.2 L under vigorous magnetic-stirring. The soil was treated with (*Paper III, V*) and without (*Paper I, II, III, V)* pH pre-adjustment. 10-30 mL of the liquid (double-distilled water and/or solutions of the chemicals) was added to 10 g of contaminated soil. Various remedial chemicals, such as hydrogen peroxide (*Paper II-V),* calcium peroxide (*Paper I*, *III, IV*), magnesium peroxide (*Paper I, II*), sodium peroxodisulphate (*Paper III*), sodium percarbonate (*Paper V*) and supplementary sources of activators, such as $FeSO_4$ x $7H_2O$ (*Paper III, V*), $Fe_2(SO_4)_3$ x $2H_2O$ (*Paper III*) and NaOH (*Paper III*) were applied.

The treatment of the 60%-watered soil was carried out for 42 d without pH pre-adjustment in a cylindrical glass reactor with a volume of 0.2 L. The soil during treatment was incubated at 20ºC (*Paper I, IV*). 10 g of the 60%-watered soil was mixed with a remedial chemical. Several remedial chemical/contaminant weight ratios were applied. Hydrogen peroxide (*Paper IV),* calcium peroxide (*Paper I, III, IV*) and magnesium peroxide (*Paper I*) were used for the treatment.

The column experiments were conducted using a 25-cm long and 8.5-cm diameter PVC pipe (*Figure 2*). The columns were packed with 1 kg of contaminated soil. Hydrogen peroxide was injected twice a day for 10 days (*Paper II*).

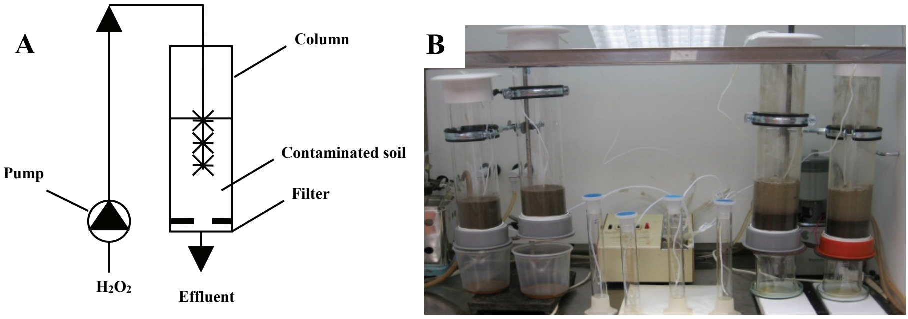

Figure 2. Column experiment: (A) schematic diagram, (B) soil treatment picture.

All of the experiments were carried out in duplicates. The experimental details and procedures are presented in the *Experimental Methods* section of *Papers I-V*. The results of the analysis are presented as the mean, with the standard deviation below 10% in all of the cases.

2.4 Analytical methods

Overviews of the analytical methods that were applied are presented in *Table 3*.

Table 3. Analytical methods

Parameter	Analytical method	Paper
pH	EPA method 9045 (1995)	I-V
Ferrous iron	The method described by Tessier et al. (1979)	I-V
Total extractable iron	The method described by Heron et al. (1994)	I-V
Ion-exchangeable iron	The method described by Tessier et al. (1979)	I-V
Organic carbon	ISO 14235 (1998)	I-V
Soil texture	ISO 14688-1,2 (2002, 2004)	I-V
Iron in the extract	Phenanthroline method (Merck, 1974)	I-V
Organic constituent concentration	Gas-chromatographic method	I-V
Residual H_2O_2	The method described by Eisenberg (1943)	I, II, III, V
Concentration of H_2O_2 in stock solution	The method described by Baxendale and Wilson (1957)	IV
Ions (F^-, Cl^-, NO_3^-, SO_4^{2-})	Ion-chromatographic method	I, II, V
Identification of constituent	Gas-chromatographic method	I, II, IV
Dehydrogenase activity in soil	ISO/FDIS 23753-1 (2002)	I, II, IV
Soil microbial respiration	ISO/DIS 16072 (2002)	I, IV
Density of oil	ISO 3675 (1998)	I
Kinematic viscosity of oil	ISO 3104 (1996)	I
Acidity of oil	ISO 6619 (1988)	I
Chemical oxygen demand	Titrimetric method (APHA, 2005)	II
Residual persulphate	The method described by Sof'ina et al. (2003)	III

All the details of analytical methods are presented in the *Experimental Methods* section of *Papers I-V*.

Matching the treatment method is an important step in effective remediation of contaminated soil. Therefore, lab-scale treatability studies are important.

3. RESULTS AND DISCUSSION

Chemicals, such as hydrogen peroxide, persulphate, percarbonate, calcium peroxide and magnesium peroxide, were applied for the treatment of contaminated soil (*Table 4*). The influence of the simultaneous application of biosurfactant (BS) and either natural microbial consortium (MO) isolated from contaminated media or chemical oxidants on the contaminants degradation was evaluated.

Table 4. Chemicals and combinations of the chemicals with BS or MO applied for the soil treatment

Contaminant	Combinations applied	Paper
Aroclor 1016	CaO_2, MgO_2	I
Aroclor 1016	H_2O_2	II
DDT, DDD, DDE	H_2O_2, $S_2O_8^{2-}$, CaO_2, $H_2O_2/S_2O_8^{2-}$, $S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/Fe^{3+}$, $S_2O_8^{2-}$/EDTA, $S_2O_8^{2-}/Fe^{2+}$/EDTA, H_2O_2/Fe^{2+}, $S_2O_8^{2-}$/NaOH, H_2O_2/Fe^{3+}, H_2O_2/EDTA, H_2O_2/Fe^{2+}/EDTA, H_2O_2/BS/EDTA, $S_2O_8^{2-}$/BS/EDTA	III
Clophen A30	H_2O_2, CaO_2, H_2O_2/EDTA, H_2O_2/Fe^{3+}/EDTA, H_2O_2/BS, CaO_2/BS, CaO_2/EDTA, MO, MO/BS, MO/H_2O_2, MO/CaO_2, MO/BS/H_2O_2, MO/BS/CaO_2, MO/EDTA/H_2O_2, MO/EDTA/CaO_2, MO/BS/EDTA/H_2O_2, MO/BS/EDTA/CaO_2	IV
p-DCB, p-C-m-Cr, p-CTh	H_2O_2, $Na_2CO_3\cdot 1.5H_2O$, H_2O_2/Fe^{2+}, $Na_2CO_3\cdot 1.5H_2O/Fe^{2+}$, $H_2O_2/Na_2CO_3\cdot 1.5H_2O$, $H_2O_2/Na_2CO_3\cdot 1.5H_2O/Fe^{2+}$	V

The optimisation of the treatment conditions (dosages and treatment time) was carried out to achieve the maximum reduction efficacy of the contaminants. Dehydrogenase activity (DHA) (*Paper I, II, IV*) and soil microbial respiration (*Paper I, IV*) were measured to assess changes in the amount of soil microflora and microbial activity during the treatment.

3.1 Chemical oxidation of contaminants in soil

3.1.1 Hydrogen peroxide for soil treatment

Contaminants (mixture of p-DCB, p-C-m-Cr, p-CTh, mixture of DDT, DDD, DDE and mixture of PCB) in the soil could degrade to some level with the addition of the chemical only (*Figure 3*), indicating the ability of the transition metal ions and the minerals of these metals present in soil to activate the oxidation reaction (*Paper II-V*). The potential of naturally occurring minerals in the soil to activate the hydrogen peroxide oxidation was indicated in several studies (Kong et al., 1998; Watts and Dilly, 1996; Teel et al., 2001, 2007), and the reaction mechanism in mineral-catalysed Fenton system was described (Watts et. al., 1990; Miller and Valentine, 1999; Huling and Pivetz, 2006).

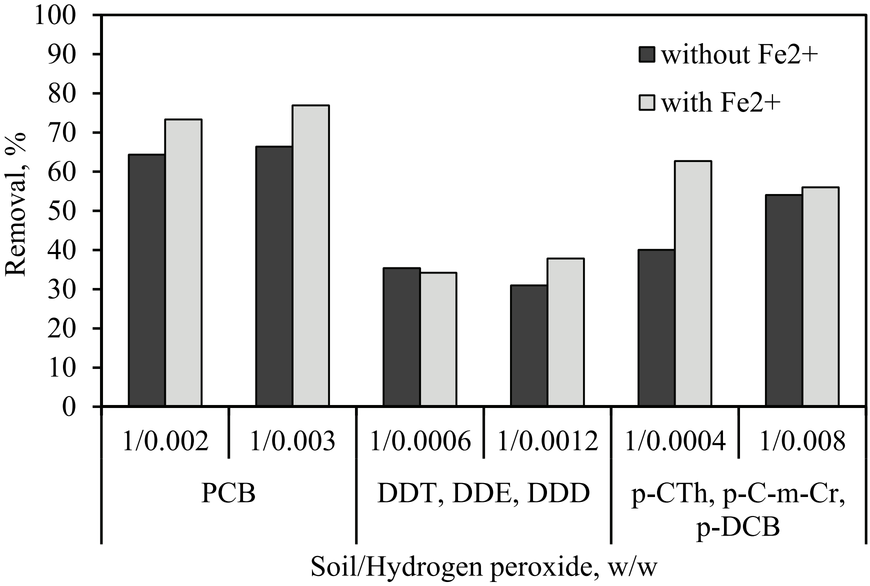

Figure 3. Contaminants removal in soil slurry at natural soil pH by a 1-d hydrogen peroxide treatment with different w/w ratios of soil/hydrogen peroxide (H_2O_2/Fe^{2+} = 10/1, w/w).

The degradation of the contaminants in the soil was incomplete and independent of the hydrogen peroxide dosage that was used. The addition of supplementary activators (Fe^{2+} and Fe^{3+}) was not always able to improve the degradation of the contaminants (*Figure 3*). The addition of a complexing agent, EDTA, for the chelating of native transition metals in soil improved the degradation of the contaminants with hydrogen peroxide *(Paper III, Figure 4; Paper IV, Figure 3*). Metal ion chelation is known to promote the chemical oxidation of contaminants at natural soil pH (Pignatello et al., 2006). The primary advantage of the metal ion complexes is the potential for the effective generation of hydroxyl radicals at near-neutral pH (Sun and Pignatello, 1992). Either chelated metal ion complex can be added as a supplement or the transition metals of the soil can be chelated by adding a complexing agent. It was hypothesised by Liang et al. (2008) that chelator-extracted native soil metals can be gradually released and serve as the activators for the persulphate oxidation of the contaminant.

The experiments in the columns that were packed with a soil of higher iron, organic carbon content and lower permeability and a soil of lower iron, organic carbon content and higher permeability showed that PCB degraded by KH_2PO_4 stabilised hydrogen peroxide in both soil matrixes; however, the efficacy of the treatment was strongly dependent on the soil characteristics. The removal of PCB (Aroclor 1016) in the sandy soil was lower than that achieved in the sandy silt soil (*Paper II, Figure 2*). In spite of the lower permeability, the higher iron content of the sandy silt soil could promote the hydrogen peroxide oxidation of the contaminants. The DHA did not change during the treatment of both sandy and sandy silt soil (*Paper II, Figure 5)*. Thus, the effective removal of the PCB-containing oil with no influence on DHA provides opportunities to apply combined oxidation with hydrogen peroxide and biodegradation with indigenous microorganisms for the soil remediation.

3.1.2 Calcium and magnesium peroxides for soil treatment

The efficacy of PCB-containing electrical insulating oil removal was improved for 1-d treatment with the increasing of calcium peroxide or magnesium peroxide dosages until it reached the optimum (*Paper I, Figure 1*). A 30-fold upsurge of the calcium or magnesium peroxide oil weight ratio from 0.005/1 to 0.15/1 increased the oil removal in soil from 36 to 70%, but further doubling of the dosage diminished oil removal to 30%. Increasing the chemical dosage led to the extensive rise in soil pH (above 8). Northup and Cassidy (2008) found that as the pH rises above the optimum, the amount of hydrogen peroxide released from calcium peroxide decreases rapidly, making the oxidation less effective. The possible reasons for oil removal retardation during a 1-d treatment with the highest dosage of calcium peroxide could be the hydrogen peroxide decomposition with the predominant production of oxygen instead of the hydroxyl radicals that are observed at high pH values (Arienzo, 2000; Northup and Cassidy, 2008). Residual hydrogen peroxide was found in soil treatment with the highest dosages of calcium and magnesium peroxides (chemical/oil of 0.3/1, w/w), which indicated that the formation of hydrogen peroxide could not be among the limiting factors for oil removal during the application. The constant amount of the available natural activator in the soil could influence the degradation of the contaminant in the soil.

Higher contaminant removal was achieved in the slurry system compared with the result obtained in the 60%-watered soil (*Paper I, III*). This improvement was most likely achieved by better desorption of the contaminant to the bulk solution and the increased dissolution rate of hydrogen peroxide. A 1-day treatment of soil in a slurry under a vigorous stirring resulted in 96% removal of Aroclor 1016, but in the 60%-watered soil with the same dosage of the chemicals applied, only 36% of contaminant removal resulted. The mode of the treatment also affected the treatment efficacy of DDT-contaminated soil (*Paper III*, *Figure 2*). A 24-h treatment of soil in slurry with calcium peroxide resulted in a higher degradation level (80%) of DDT mixture than the 50% achieved by the treatment of the 60%-watered soil. The influence of the hydrogen peroxide solid carrier dissolution rate on contaminant degradation was also observed in the studies of Arienzo (2000), Pignatello et al. (2006), Northup and Cassidy (2008), and Xu et al. (2011).

The prolongation of the treatment time at lower chemical dosages (chemical/oil of 0.005/1, w/w) from 1 to 21 d allowed the removal of 96% of the contaminant in the 60%-watered soil (*Paper I*). Furthermore, prolonging the treatment time from 1 to 5 d removed approximately 10% of PCB (*Paper IV)*. The improved removal of the contaminant with increased treatment time can be caused by the auto-regulated release of hydrogen peroxide from the solid carrier that reduces disproportionate hydrogen peroxide consumption. No substantial changes in the amount of soil microflora and microbial activity within 21 d of treatment by either calcium or magnesium peroxide moderate dosages application and in the soil without the peroxide addition (*Paper I, Table 3*) were found. A slight increase in oxygen consumption was observed after 21 d incubation. This rise in the activity of indigenous microorganisms in treated soil was possibly achieved by the oxygen release, increase in substrate solubility and improvement of nutrients availability to the microbial cell.

3.1.3 Persulphate for soil treatment

DDT and PCB in soil could degrade to some level with the addition of only persulphate, indicating a possible ability of natural soil minerals or transition metals to initiate chemical oxidation (*Figure 4*).

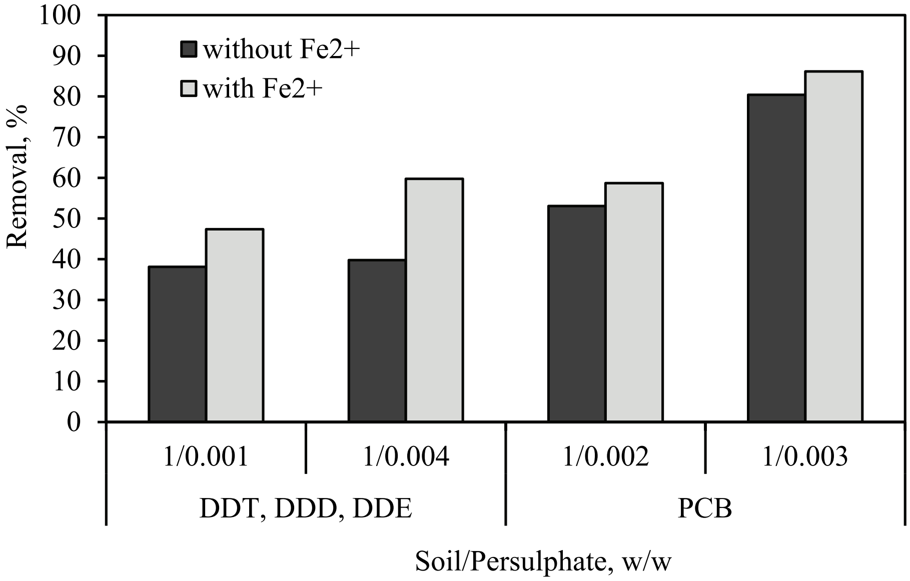

Figure 4. Contaminants removal in soil slurry with different w/w ratios of soil/persulphate by a 1-d treatment ($S_2O_8^{2-}/Fe^{2+}$=10/1, w/w).

Slightly higher, if any improvement in the degradation level, was achieved with the addition of supplementary ferrous iron (*Figure 4*). Consumption of persulphate was nearly twice as high as in the soil treated with only persulphate, making the activation with ferrous iron often useless. Ferric iron was not an effective activator of the persulphate oxidation also (*Paper III, Figure 3*). The addition of a complexing agent EDTA resulted in higher removal of the contaminant than with the persulphate only (*Paper III*). Pignatello and Baehr (1994) hypothesised that chelator-extracted native soil metals can be slowly released and serve as the activators for the persulphate oxidation of the contaminant. The addition of BS improved the degradation of DDT with persulphate by the enhanced desorption of the contaminant to the liquid phase, making it available to the oxidising agents. The oxidation was dependent on the biosurfactant dosage (*Paper III, Figure 7*). The addition of NaOH to increase the pH over 11, resulted in higher DDT degradation levels compared with that achieved by the treatment at natural soil pH (*Paper III, Figure 6*). Strong alkaline condition was also suggested in other studies by Tsitonaki et al. (2010), Ahmad et al. (2010), Block et al. (2004).

Activation of persulphate with hydrogen peroxide improved the degradation of DDT *(Paper III, Figure 1*). It was hypothesised by Block et al. (2004) that the combined usage of hydrogen peroxide and persulphate may provide a multi-radical attack mechanism presented in the study of Tsao and Wilmarth (1960), yielding a higher efficacy in destroying contaminants or allowing recalcitrant compounds to be more readily degraded.

3.1.4 Percarbonate for soil treatment

Although treatment with percarbonate in a study by Rivas et al. (2010) has indicated that metoprolol in aqueous solution has the same oxidising power as liquid hydrogen peroxide, a 24-h soil treatment with percarbonate in the present study led to the improved degradation of p-DCB, p-C-m-Cr and p-CTh compared to that obtained by the treatment with liquid hydrogen peroxide. It can be assumed that several other reactions besides hydrogen peroxide oxidation were able to proceed. For example, in a study by Regino and Richardson (2007), kinetic and spectroscopic studies of the bicarbonate-catalysed oxidation of organic sulphides have strongly supported the role of peroxymonocarbonate (HCO_4^-) as the oxidant in bicarbonate-activated hydrogen peroxide solutions. In a study by Xu et al. (2011), bicarbonate anions have also been identified as efficient activators of the hydrogen peroxide oxidation of some organic pollutants, including 4-chlorophenol, providing an efficient transition-metal-free treatment method.

Increasing percarbonate dosage slightly improved the treatment efficacy (*Paper V, Figure 1*). A lack of available activators in the soil may also limit the effective degradation of the contaminant. Increasing ferrous iron dosage did not improve the degradation at the lower ratio of contaminant/H_2O_2 =1/0.1 (w/w); however, at the higher ratios of contaminant/H_2O_2=1/1 (w/w), the removal efficacy was considerably increased (*Paper V, Figure 2*). This can be explained by the carbonates' ability to scavenge the excess of hydroxyl radicals formed during the activation of hydrogen peroxide by supplemental ferrous iron addition. Soil pH increased after the treatment with percarbonate. This can reduce the activation efficacy as ferrous iron oxidises to ferric iron. Lower enhancement in the treatment efficacy at the lower ratios of contaminant/H_2O_2 could also be explained by the excessive iron that provided conditions for the increased quenching of oxidising agents, reducing the contaminant degradation efficacy as a result (Barb et al., 1951). Thus, it is important to optimise not only the hydrogen peroxide/contaminant ratio but also the hydrogen peroxide/transition metal activator ratio.

The initial soil pH (*Paper V, Table 1*) was higher than the optimum pH range of 2-4 identified (Sedlak and Andren, 1991; Ghaly et al., 2001) for the chemical oxidation of chlorinated aromatics, using the hydrogen peroxide oxidation processes in water. Contrary to the soil treatment with liquid hydrogen peroxide, the percarbonate treatment of the soil at an initial pH of 2.5 resulted in no improvement in contaminant degradation (*Paper V, Figure 4*). Percarbonate dissolves in water and may yield not only hydroxyl radicals but also several other oxidation species that may be more stable at near-neutral pH values (Zuo et al., 1999; Yao and Richardson, 2000; Regino and Richardson, 2007). For example, in the study of Yao and Richardson (2000) on bicarbonate activated hydrogen peroxide, a maximum catalytic efficacy for the oxidation of organic sulphides in aqueous solution was in the pH range of 7-9.

3.2 Effect of biosurfactants addition on the chemical and/or biological treatment of contaminated soil

The addition of BS improved the degradation of total DDT with persulphate and hydrogen peroxide (*Paper III, Figure 7*). The chemical oxidation of the contaminant was found to be dependent on the BS dosage. The optimal dosage of BS differed for combined treatment utilising hydrogen peroxide and for that utilising persulphate.

The combined chemical, using hydrogen peroxide, and biological treatment of PCB-contaminated soil (*Paper IV*) was more effective than the treatment with MO only or with both MO and BS. It was found that higher degradation of the contaminants was achieved after the application of BS (*Paper IV, Figure 3*). BS has higher biodegradability and biocompatibility, while EDTA is more stable, having lower biodegradability and higher absorption ability on soil particles (Tokunaga, 1996; Herman et al., 1995). This makes the usage of BS more preferable for soil decontamination by combined chemical and biological treatment. Solid carrier of hydrogen peroxide, calcium peroxide, improved the degradation of PCB-contaminated soil with MO. BS addition to the system, along with MO and calcium peroxide, resulted in higher microbial respiration, DHA and oil removal than in the case of EDTA addition (*Paper IV, Figure 3*). Soil pH did not change notably during the treatment. Slight pH variation was observed after adding the remedial chemicals, however, after 42 days of the treatment, the pH was near its initial value, showing the strong buffering capacity of the soil.

The process integration achieved by the joint application of BS, the oxidising chemical in moderate dosages and microbial consortium could be a promising option for soil decontamination resulting in improved treatment efficacy. Among the reasons for the increased efficacy of the combined chemical-biological treatment with the BS addition could be desorption and solubilisation of the contaminants by the BS and enhancement of the chemical oxidation by increasing their availability. A possible effect of BS on the chemical-biological treatment of contaminated is illustrated in *Figure 5 of Paper V*.

CONCLUSIONS

The results of the study can be summarised as follows:

1. New remedial chemicals, such as calcium peroxide, magnesium peroxide, percarbonate and persulphate, could be utilised as effective alternatives to hydrogen peroxide for the treatment of contaminated soil at natural soil pH values. The contaminant removal efficacy was found to be strongly dependent on the dosage of the chemical, treatment time and treatment manner (the treatment of the vigorously mixed soil slurry, the soil in soil packed columns or the 60%-watered, once-pre-mixed soil) and the soil characteristics. The contaminant in the soil could degrade with the addition of the remedial chemicals only, indicating the ability of transition metals and minerals of these metals presented in soil to activate the oxidation reaction at natural soil pH. However, the degradation of contaminants in soil was often incomplete and independent of the chemical dosages used. Properly selected activator aids were found to be important for effective treatment of contaminated soil.

2. A novel approach considering the utilisation of a prolonged treatment time with the moderate addition of solid hydrogen peroxide carriers (calcium or magnesium peroxides) instead of the high dosages and short treatment time that are usually used is recommended to reduce non-productive oxidant decomposition and to promote the coexistence of chemical and biological oxidation of contaminants.

3. The addition of BS stimulated the degradation of the contaminants with calcium peroxide, hydrogen peroxide and persulphate. Thus, combined treatment with the application of BS for increased availability and solubility of both the contaminant and the transition metals of the soil and the chemicals for the oxidation of contaminants could be a new and promising option for contaminated soil remediation.

4. Novel treatment methods for soil decontamination with the joint application of the BS, MO and oxidising chemicals in moderate dosages not only improved the treatment efficacy but could increase soil respiration and dehydrogenase activity above that which obtained by the application of the microbial consortium alone, indicating the stimulation of microflora by process integration.

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Peroxygen compounds and new integrated processes for chlorinated hydrocarbons degradation in contaminated soil

ABSTRACT

Chemical oxidation is a promising innovative technology that degrades an extensive variety of hazardous compounds for soil remediation at waste disposal and spill sites. Such novel remedial chemicals as persulphate, percarbonate, and calcium, magnesium peroxides can be used to solve apparent disadvantages of activated hydrogen peroxide application, including violent exothermic reactions, handling problems associated with the need for pH control and oxidant rapid consumption. In addition to the chemical oxidation of the contaminant, the application of optimised chemical dosages can potentially enhance the aerobic biodegradation of contaminants in soil by indigenous microorganisms. A well-executed chemical to biological treatment approach can result in considerable contaminant reduction and may yield substantial cost savings. Another new promising approach could be the application of microbial surfactants (biosurfactants) to integrated chemical and biological oxidation processes, where biosurfactants may act as oxidation stimulators by releasing contaminants that are adsorbed in soil into the liquid medium and, thus, increase their availability to oxidising agents and microorganisms.

Chlorinated hydrocarbons as soil contaminants are the target compounds of the present research due to their hazardous properties and the vast number of emission sources.

The main objectives of the present research are

- to find effective treatment methods using peroxygen chemicals (hydrogen peroxide, persulphate, percarbonate, calcium and magnesium peroxides) for the remediation of chlorinated hydrocarbons contaminated soil;
- to test different activation aids (supplemental application of non-chelated/chelated ferrous and ferric iron, chelation of natural transition metals of soil, base activation of persulphate, combined application of persulphate and hydrogen peroxide, application of acidic pH conditions to sustain the persulphate and hydrogen peroxide activation processes);
- to optimise treatment conditions (dosages, treatment time and treatment mode) to achieve the maximum reduction efficacy of contaminant and to minimise stress on soil bacteria after the application of strong oxidants of peroxygen family and to support subsequent biodegradation of contaminants in soil by indigenous microorganisms;
- to develop a new strategy of process integration by the joint application of biosurfactants and combined chemical and/or biological (using a natural consortium of microorganisms-hydrocarbons destructors) treatment for soil decontamination.

Soil samples were artificially contaminated with PCB-containing oil (Aroclor 1016 and Clophen A30), a commercial DDT mixture and a mixture of chlorinated aromatic hydrocarbons, such as p-dichlorobenzene, p-chloro-m-cresol and p-chlorothymol. Soil treatment was carried out in three different ways: in slurry under batch condition, in a 60%-watered soil, and in columns.

It was found that calcium peroxide, magnesium peroxide, percarbonate and persulphate could be utilised as an effective alternative to hydrogen peroxide for the treatment of contaminated soil at natural soil pH values. The contaminant removal efficacy was strongly dependent on the dosage of the chemical, selected activation aid, treatment time, treatment manner and soil characteristics. The contaminant in the soil could degrade with the addition of the remedial chemicals only, indicating the ability of transition metals and the metal minerals present in the soil to activate the oxidation reaction at natural soil pH. A novel approach considering the utilisation of a prolonged treatment time with the moderate addition of the solid hydrogen peroxide carriers (calcium or magnesium peroxides) could be recommended to reduce non-productive oxidant decomposition and to promote the coexistence of chemical and biological oxidation of contaminants.

The addition of the biosurfactant stimulated the degradation of the contaminants with calcium peroxide, hydrogen peroxide and persulphate. Thus, combined treatment with the application of the biosurfactant for increased availability and solubility of both the contaminant and transition metals present in soil and the chemicals for the oxidation of contaminants could be a promising option for the remediation of contaminated soil. A novel option for soil decontamination achieved by the joint application of the biosurfactant, microorganisms and oxidising chemicals in moderate dosages not only improved the treatment efficacy but could increase the soil microbial respiration and dehydrogenase activity above that which was obtained by application of the microbial consortium alone, indicating stimulation of microflora by process integration.

Peroksü-ühendite ja uute integreeritud protsesside kasutamine kloorsüsivesinike lagundamiseks saastatud pinnases

KOKKUVÕTE

Keemiline oksüdatsioon peroksü-ühenditega on perspektiivne innovatiivne tehnoloogia erinevate ohtlike saasteainete lagundamiseks jäätmete ladestus- või lekkealade pinnases. Katalüütilisel oksüdatsioonil vesinikperoksiidiga on sageli puuduseks tormiline eksotermiline reaktsioon, vajadus reguleerida pH-d ja oksüdandi kiire tarbimine. Uute taastamiskemikaalide, nagu näiteks, persulfaadi, perkarbonaadi, kaltsium- ja magneesiumperoksiidide, kasutamisel on võimalik neid probleeme vältida. Lisaks saasteainete keemilisele oksüdatsioonile on pinnase töötlemisel, kasutades optimaalseid kemikaalide doose, võimalik parandada ka järgnevat saasteainete aeroobset biooksüdatsiooni pinnases seal oleva mikroorganismide koosluse toimel. Keemilise ja bioloogilise töötluse kombineerimise tulemusena on võimalik oluliselt vähendada saasteainete sisaldust pinnases ja minimeerida kulutusi. Veel üks paljulubav uus meetod on integreeritud meetod – keemiline ja biokeemiline oksüdatsioon koos biopindaktiivsete ainete kasutamisega, milles viimased võivad toimida oksüdatsiooni stimulaatoritena, soodustades saasteaine desorptsiooni vedelfaasi ja sellega suurendades saasteaine kättesaadavust oksüdeerivatele ainetele ja mikroorganismidele.

Uurimistöö sihtsaasteaineteks on kloorsüsivesinikud nende ohtlike omaduste ja paljude emissiooniallikate tõttu.

Antud uurimustöö põhieesmärgid on:

- leida efektiivne meetod kloorsüsivesinike lagundamiseks pinnases kasutades peroksükemikaale (persulfaat, perkarbonaat, kaltsium- ja magneesiumperoksiidid);
- eksperimentaalselt uurida erinevaid aktiveerimise võimalusi (täiendava mitte-kelaatse/kelaatse kahe- ja kolmevalentse raua kasutamine, pinnase siirdemetallide kelaatumine, persulfaadi kasutamine kõrge pH juures, persulfaadi ja vesinikperoksiidi kombineeritud kasutamine, persulfaadi ja vesinikperoksiidiga töötluse teostamine happelises keskkonnas aktiveerivate omaduste säilitamiseks);
- optimeerida töötlemistingimusi (doose, töötlemisaega ja -viisi), et saavutada maksimaalne saasteaine eemaldumine ja vähendada pinnase bakterite stressi tugevate oksüdeerijate kasutamisel ja soodustamaks järgnevat biolagundamist;
- töötada välja uued strateegiad pinnase taastamiseks kombineerides biopindaktiivsete ainete kasutamist keemiliste ja/või bioloogiliste meetoditega.

Eksperimentides kasutatud pinnaseproovid saastati kunstlikult polüklooritud bifenüüle sisaldava õliga (Aroclor 1016 ja Clophen A30), kaubandusliku DDT

seguga, klooritud aromaatseid süsivesinikke (p-diklorobenseeni, p-kloro-m-kresooli ja p-klorotümooli) sisaldava seguga. Pinnase töötlemist viidi läbi kolmel erineval viisil: intensiivselt segatud pinnase suspensioonis, 60%-niiskusega pinnases ja läbivooluga täidiskolonnides.

Uuringute tulemusena leiti, et kaltsium- ja magneesiumperoksiidi, perkarbonaati ja persulfaati on võimalik kasutada vesinikperoksiidi efektiivse alternatiivina saastatud pinnase töötlemisel loomuliku pH juures. Pinnase taastamise efektiivsus sõltus suurel määral taastamiskemikaali doosist, valitud aktivaatorist, töötlemisajast ja -viisist ning pinnase omadustest. Selgitati, et pinnases sisalduvaid saasteaineid on võimalik lagundada ka ainult taastamiskemikaalidega, mis näitab, et pinnases olevad siirdemetallid ja nende ühendid on võimelised pinnase loomuliku pH juures aktiveerima oksüdatsiooni. Tehti kindlaks, et oksüdeerijate mitte-radikaalilise lagunemise vältimiseks ning saasteainete samaaegse keemilise ja biokeemilise oksüdatsiooni soodustamiseks tuleks kasutada pikemat töötlemisaega ja mõõdukaid tahkete peroksü-ühendite (kaltsium- ja magneesiumperoksiid) doose.

Eksperimentidest selgus samuti, et biopindaktiivsete ainete kasutamine lisanditena pinnase töötlemisel kaltsiumperoksiidi, vesinikperoksiidi ja persulfaadiga kiirendas saasteaine lagundamist. Seega võib kombineeritud töötlemine, milles on ühendatud biopindaktiivsete ainete kasutamine parandamaks saasteaine ja pinnase siirdemetallide desorptsiooni ja kättesaadavust ning peroksü-ühendite kui saasteaineid oksüdeerivate ühendite kasutamine, olla perspektiivne võimalus saastatud pinnase tervendamisel (remediatsioonil).

Töö tulemusena näidati, et uueks paljutõotavaks pinnase taastamise meetodiks on integreeritud meetod – keemiline oksüdatsioon peroksü-ühendite mõõdukate doosidega koos samaaegse biokeemilise oksüdatsiooni ja biopindaktiivsete ainete kasutamisega, kusjuures koosmõju tulemusena paraneb nii saasteainete lagundamise efektiivsus kui ka pinnase mikroobne hingamine ja aktiivsus.

APPENDIX A. PUBLICATIONS

PAPER I

Goi, A., Viisimaa, M., Trapido, M., Munter, R. (2011). Polychlorinated biphenyls-containing electrical insulating oil contaminated soil treatment with calcium and magnesium peroxides. – *Chemosphere*, 82, 1196-1201.

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Technical Note

Polychlorinated biphenyls-containing electrical insulating oil contaminated soil treatment with calcium and magnesium peroxides

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ABSTRACT

Calcium and magnesium peroxides were applied for the treatment of soil contaminated by polychlorinated biphenyls-containing electrical insulating oil (Aroclor 1016). The removal of PCB-containing electrical insulating oil was achieved with the addition of either calcium peroxide or magnesium peroxide alone and dependent on dosages of the chemical. A 21-d treatment of 60% watered soil with the moderate addition (chemical/oil weight ratio of 0.005/1) of either calcium peroxide or magnesium peroxide resulted in nearly complete (96 ± 2%) oil removal, unsubstantial increase in soil pH and almost no changes in oxygen consumption and dehydrogenase activity, making it suitable for the soil decontamination.

1. Introduction

Polychlorinated biphenyls (PCBs) are toxic and persistent pollutants that have been released into the environment for decades. PCBs have primarily been used in electrical equipment, such as capacitors and transformers, in which their insulating properties and ability to withstand high temperatures prove useful. Thus, electrical insulating oil containing PCBs could enter the environment during salvage and repair operations, as it is dumped, spilled, or leaked from electrical units into the ground. PCBs have also found applications in numerous other contexts, for example, as components in PVC plastics, paints, adhesives, lubricants, sealants and pressure sensitive (carbonless) copy paper. Thus, due to the vast number of sources and environmentally hazardous properties of PCBs the implementation of effective treatment methods for soil decontamination is required.

Chemical oxidation is a promising degradation method for an extensive variety of hazardous compounds for the decontamination of soil at waste disposal and spill sites. There are several studies (Carberry and Yang, 1994; Aronstein and Rice, 1995) where chemical oxidation by catalyzed hydrogen peroxide oxidation process was effectively used for PCB-contaminated soil treatment. However, the application of calcium peroxide was found to be more efficient for degrading contaminants in soil than the direct hydrogen peroxide application (Northup and Cassidy, 2008) demonstrating the efficacy of this chemical for tetrachloroethylene (Northup and Cassidy, 2008), petroleum hydrocarbons (Ndjou'ou and Cassidy, 2006), polycyclic aromatic hydrocarbons (Bogan et al., 2003) and 2,4,6-trinitrotoluene (Arienzo, 2000) contaminated soil treatment. The use of this chemical can solve apparent disadvantages in the direct application of hydrogen peroxide; including violent exothermic reaction, handling problems associated with the need for pH control, and a rapid consumption of oxidant.

Calcium peroxide has been mostly applied as the stimulator of aerobic bioremediation of contaminated soil (Cassidy and Irvine, 1999) and groundwater (Kao et al., 2001; Kao et al., 2003; Liu et al., 2006) for oxygen generation (Eq. (1)) during slow decomposition in contact with water. However, it was found (Arienzo, 2000; Northup and Cassidy, 2008) that calcium peroxide, as the source of hydrogen peroxide (Eq. (2)), is also involved in chemical oxidation of contaminants in soil and water. Hydrogen peroxide generated from calcium peroxide over a wide pH range (Northup and Cassidy, 2008) reacts through the direct oxidation of contaminants or through the formation (Eq. (3)) of hydroxyl radicals and other (Watts et al., 1999) oxidative/reductive species.

$$CaO_2 + H_2O \rightarrow 0.5O_2 + Ca(OH)_2 \quad (1)$$

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (2)$$

$$H_2O_2 + \text{activator}^{*} \rightarrow OH^{\cdot} + OH^{-} \quad (3)$$

*activator – transition metal ions and minerals.

The transition metals (ferrous, ferric iron, etc.) and their minerals (hematite, goethite, magnetite, ferrihydrite, etc.) present in soil

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can initiate hydrogen peroxide decomposition without addition of the supplementary activator (Watts et al., 1992). While iron minerals can catalyze the Fenton reaction (Eq. (3)), they are lees reactive than soluble iron, especially when the pH is not lowered (Teel et al., 2001). The requirement for acidic conditions needed to keep Fe(III) soluble limits the utility of Fenton's reagent for treating contaminated soil at natural soil pH that usually lies in the range of 4–8 (Pignatello et al., 2006). The chelation of the metal ions in soil can promote the chemical oxidation of contaminants in a wider pH range. The primary advantage of the metal ions complexes is the potential for effective generation of hydroxyl radicals at near-neutral pH (Sun and Pignatello, 1992). Organic substances (organic acids, amino acids and hydroxamate siderophores) in soil either applied or produced by plants or microorganisms are the natural chelating agents. There are several studies (Ndjou'ou and Cassidy, 2006; Northup and Cassidy, 2008) where the application of the supplementary chelated iron or a chelating agent for the chelation of the native iron of soil was found to be effective in order to sustain the chemical oxidation of contaminants by the modified-Fenton chemistry utilizing calcium peroxide at the basic pH conditions. There are also several studies (Arienzo, 2000; Bogan et al., 2003) where contaminants in soil could degrade in a wide (from 5.8 up to 12) pH range with the addition of calcium peroxide alone utilizing the potential ability of natural soil catalyst to activate the reaction of hydrogen peroxide decomposition.

Low solubility of magnesium and calcium peroxides allows continuous release of oxygen and hydrogen peroxide for a long time with minimal site disruption. However, the release of oxygen and hydrogen peroxide depends upon many factors including type, pH and buffering capacity of soil, type of contaminants and their concentration, as well as, the presence of other organics or metals in the soil (Duffy et al., 2006). Calcium and magnesium peroxides have also been used (Goi and Trapido, 2010) as activators for stronger chemicals, such as persulfate ion with the multi-radical attack mechanism provided by hydroxyl and sulfate radicals (Block et al., 2004) for improving soil decontamination.

In the present study the application of calcium and magnesium peroxides for the treatment of soil contaminated by PCB-containing electrical insulating oil (Aroclor 1016) on a laboratory scale was performed. The optimization of the treatment conditions (dosages, treatment time and treatment mode) was carried in order to achieve the maximum reduction efficacy of oil. Consumption of oxygen and dehydrogenase activity (DHA) was measured in order to assess changes in the amount of soil microflora and microbial activity during either calcium peroxide or magnesium peroxide application. The outcome of the research provides a scientific basis for practical application of the effective method utilizing calcium and magnesium peroxides for the treatment of soil contaminated by PCB-containing electrical insulating oil.

2. Materials and methods

2.1. Soil sample preparation and characterization

Natural topsoil (0–20 cm) was dried over-night at 30 °C in a circulating air drying oven before the spiking and sieved through a 2.0 mm sieve using a Retsch (AS 200) digital sieve shaker. Several characteristics of the soil are presented in Table 1. Ferrous iron and ion-exchangeable Fe(II) fraction were extracted according to the procedure presented by Tessier et al. (1979). Total extractable iron in the soil was extracted according to Heron et al. (1994). Iron in the extracts was measured photometrically at 492 nm by phenanthroline method (Merck, 1974). Soil pH was measured according to EPA method 9045C (1995) using a digital pH meter (CG-840, Schott) equipped with a Mettler Toledo InLaB 412 electrode.

Table 1
Several properties of soil.

Parameter, unit	Value (mean ± standard deviation)
pH	5.2
Ferrous iron, g kg^{-1} of soil	1.9 ± 0.5
Total extractable iron, g kg^{-1} of soil	12.1 ± 0.9
Ion-exchangeable Fe(II) fraction, mg kg^{-1} of soil	2.0 ± 0.3
Organic carbon, mg kg^{-1} of soil	460 ± 30
Sand, %	45.5
Silt, %	52
Clay, %	2.5
Cl^-, mg kg^{-1} of soil	8.8 ± 0.2

Organic carbon of the soil was determined by sulfochromic oxidation (ISO 14235, 1998). The identification of soil texture was based on the principles established by ISO 14688-1,2 (2002, 2004) using a laser scattering particle size distribution analyzer (LA-950, Horiba). The texture of the soil was identified as sandy silt. Chloride ion in the soil filtrate was measured using an ion chromatograph (761 Compact IC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm id) analytical column. Chloride ion formed, as a result of organically bounded chlorine mineralization during the treatment, was calculated taking into account the chloride ion content in the initial soil sample.

2.2. Soil contaminant

Electrical insulating oil, identified as Aroclor 1016 – commercial formulation of light PCBs congers (12.9% of 2-ring PCBs, 66.0% of 3-ring PCBs, 21.0% of 4-ring PCBs and 0.1% of 5-ring PCBs), was obtained from an old capacitor. The characterization of the oil was carried out using a HP-6890 GC with a HP 5972A mass spectrometer (MS). Two microliters were injected in a bonded Supelco Equity-5 (5% diphenyl)-dimethylsiloxane capillary column. The GC–MS temperature program was as follows: the temperature was held at 80 °C for 1 min, then increased at the rate of 30 °C min^{-1} up to 150 °C, 4 °C min^{-1} up to the temperature of 250 °C and 10 °C min^{-1} up to the temperature of 300 °C. Injector and detector temperatures were 250 and 280 °C, respectively.

Electrical insulating oil used for the soil spiking had a density of 1.386 g cm^{-3} (measured according to ISO 3675, 1998) and a kinematic viscosity of 51.2 cSt (measured according to ISO 3104, 1996). Acidity of the oil measured according to ISO 6619 (1988) was zero indicating that the oil was not oxidized.

Dry soil was artificially spiked with the PCB-containing oil under continuous mixing for 5 h to ensure the contaminant distribution homogeneity and, hence, a better reproducibility in repeated experiments. The initial concentration of Aroclor 1016, verified by the analysis of eight replicates, was 39 ± 1 g oil kg^{-1} of dry soil. Oil recovery from the soil was 91%.

2.3. Soil treatment with calcium and magnesium peroxides

Magnesium peroxide (MgO_2 and MgO mixture, powder, commercially available product) and calcium peroxide (CaO_2 and $Ca(OH)_2$ mixture, powder, 200 mesh (0.075 mm), commercially available product), purchased from Aldrich, were applied for the soil treatment. The contents of CaO_2 in calcium peroxide and MgO_2 in magnesium peroxide were 76.4 ± 0.1% (with 17.0 ± 0.1% w/w of available oxygen) and 11.6 ± 0.1% (with 3.3 ± 0.1% w/w of available oxygen), respectively. The concentrations of active compounds, CaO_2 and MgO_2, in the technical products were determined by the titration of either calcium peroxide or magnesium peroxide acidic (6% HCl and 14% H_3PO_4) solution by 0.5 N $KMnO_4$.

Ten grams of moist (with 60% of double-distilled, autoclaved water) soil were mixed with calcium peroxide or magnesium peroxide technical product (powder) and then incubated without pH pre-adjustment and stirring in the cylindrical glass reactor with a 0.2-L of volume for different treatment periods. Several calcium peroxide or magnesium peroxide/oil weight (w/w) ratios were applied in these experiments. Control soil was prepared by autoclaving the soil (125 °C, 1 h) twice with 3 d interval (Palmroth et al., 2006).

The chemical treatment of contaminated soil in slurry (10 g of soil with 30 mL of double-distilled water (1/3, w/v) and certain amount of either calcium peroxide or magnesium peroxide powder) was carried out (without pH pre-adjustment) under a vigorous (300 rpm) magnetic-stirring in a cylindrical glass reactor with a 0.2-L of volume for 24 h. Chemical/oil weight ratio of 0.005/1 was applied in the soil slurry experiments. All experiments were carried out in duplicates at 20 ± 1 °C. Results are presented with ± standard deviation of the mean.

Residual hydrogen peroxide in soil filtrate treated by titanium sulfate with pertitanic acid formation was measured photometrically at 410 nm (Eisenberg, 1943). The release of hydrogen peroxide from either calcium peroxide or magnesium peroxide dissolution was tested in buffered (pH 5.5) double-distilled water under a vigorous stirring (300 rpm) for 24 h. Phosphate (1.5 M KH_2PO_4 and 0.2 M $K_2HPO_4 \cdot 3H_2O$) buffer solution was used in this experiment.

2.4. Extraction and determination of electrical insulating oil

In order to evaluate the influence of $Ca(OH)_2$ on extractability of PCBs from the soil after the treatment with the highest (calcium peroxide/oil ratio of 0.3/1, w/w) dosage the pH was adjusted back to the initial (Table 1) soil pH by adding (Arienzo, 2000) 10% H_3PO_4. Then the solid phase was dried with anhydrous Na_2SO_4. Dried soil with the filter (slurry experiments) was soaked in 10 mL of *n*-hexane (Fischer, analytical grade) and placed for the extraction to a laboratory reciprocal shaker (Eplan 358S) over-night. Then, a vortex (IKA, Genius3) extraction procedure three times (10 mL of hexane each time) per 3 min was used. Joined hexane extracts were mixed with internal standard (1/1). The internal standard was tridecane dissolved in *n*-hexane with the concentration of 3.3 g L^{-1}. Similar oil extraction procedure was applied for the initial untreated soil.

The measurement of Aroclor 1016 was carried out using a FocusGC, Finnigan GC-FID (Thermo Electron Corporation). Two microliters were injected splitless in a crossbond 100% dimethylpolysiloxane capillary column RTX-1 (30 m × 320 μm id × 0.25 μm film thickness). The injector temperature was set to 200 °C. The GC temperature program started at 40 °C, the initial temperature was held for 1 min then increased by 10 °C min^{-1} to 140 °C, followed by 4 °C min^{-1} increased to 230 °C and the final temperature was held for 2 min. The detector temperature was 200 °C. The velocity of carrier gas (nitrogen) was 1 mL min^{-1}. External standard was prepared by dissolving Aroclor 1016 in *n*-hexane. Quantification was based on the area count obtained for the merged peaks with the peak start of 17 min and peak end of 35 min. The detection limit of the method was 30 mg oil L^{-1} of hexane that corresponds to 90 mg oil kg^{-1} of dry soil. Oil concentration in soil was calculated per dry weight. Dry matter in soil samples was determined by oven drying at 105 °C. The GC-FID analyses of un-spiked soil did not show any content of contaminants.

2.5. Soil microbial respiration and dehydrogenase assay

Soil microbial respiration was determined (ISO/DIS 16072, 2002) by oxygen consumption using a Lovibond OxiDirect closed system volumetric respirometer. The humidity of the sample was kept up to 60% and the sample was incubated at 20 °C in the thermostatically controlled cabinet for a 28-d incubation period. The reading of the results was performed every 24 h.

DHA in soil was measured by triphenylformazan (TPF) production according to ISO/FDIS 23753-1 (2002). Two grams of moist soil were mixed with 5 mL of 2,3,5-triphenyltetrazolium chloride dissolved in Trizma hydrochloride buffer solution (0.1 M, pH 7.4) or (control sample) with 5 mL of Trizma hydrochloride buffer solution only and incubated at 30 °C in dark for 24 h. TPF produced was extracted with acetone (16 mL) at a laboratory shaker (Eplan 358S) for 1 h and measured photometrically (Heλios UV–Vis spectrophotometer, Thermo Electron Corporation) at 546 nm.

3. Results and discussion

3.1. Aroclor 1016 removal in soil

The removal of PCB-containing electrical insulating oil, Aroclor 1016, in 60% watered, once-pre-mixed soil utilizing different dosages of either calcium peroxide or magnesium peroxide and different (1 and 3 d) treatment time is presented in Fig. 1. Since the treated soil contained a lot of native iron (Table 1) that could be potentially chelated by natural soil chelating agents and in order to utilize the ability of calcium and magnesium peroxides to release H_2O_2 slowly that reducing its non-productive decomposition usually achieved (Miller et al., 1996) during the non-supplemented direct hydrogen peroxide application, addition of calcium and magnesium peroxides alone for the soil treatment was tested.

As can be seen in Fig. 1, the removal of PCB-containing electrical insulating oil in 60% watered, once-pre-mixed soil was achieved with the addition of either calcium peroxide or magnesium peroxide alone and dependent on dosages of the chemicals. The oil removal efficacy considerably increased for a 1-d treatment with the increasing of either calcium peroxide or magnesium peroxide dosage until it reached the optimum. A 30-fold upsurge of calcium peroxide/oil weight ratio from 0.005/1 to 0.15/1 increased the oil removal in soil from 36 ± 3 to 70 ± 1%, respectively. The increase in the soil pH, achieved by the release of $Ca(OH)_2$ (Eqs. (1) and (2)), from initial 5.2 up to 8.7 at the chemical/oil ratio of 0.15/1 and up to 7 at the lower dosages of the chemicals was observed (Fig. 2). The optimum pH found in the study of Northup and Cassidy (2008) for the treatment with calcium peroxide in

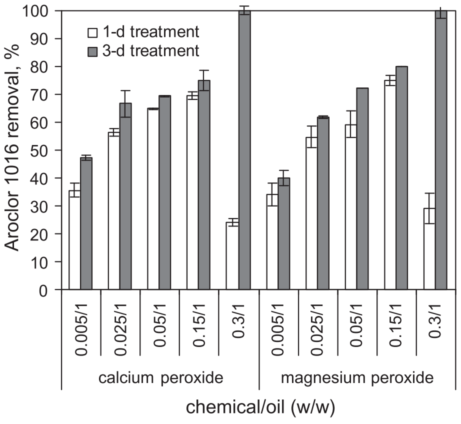

Fig. 1. Aroclor 1016 oil (initial concentration of 39 ± 1 g oil kg^{-1} of dry soil) removal (mean ± standard deviation) in 60% watered soil by 1- and 3-d treatments with different w/w ratios of chemical/oil.

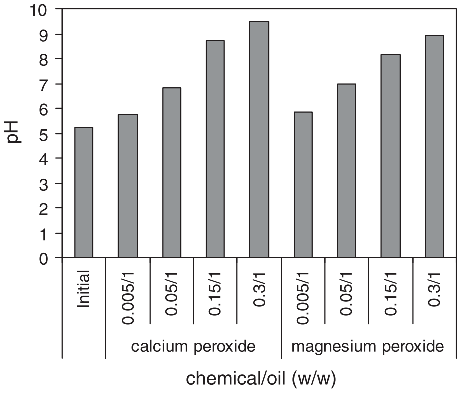

Fig. 2. pH of the soil after a 1-d treatment with different w/w ratios of chemical/oil.

modified-Fenton chemistry was 8. Below this pH the rate of hydrogen peroxide release was found (Northup and Cassidy, 2008) to be too high that may cause its excessive disproportionation diminishing contaminant removal in soil. Thus, pH conditions created during the soil treatment with different dosages of the chemical could explain the difference in contaminant removal. The further doubling of calcium peroxide dosage (calcium peroxide/oil ratio increased from 0.15/1 to 0.3/1) both considerably increased the soil pH (up to 9.5) and, as a result substantially diminished (up to 28 ± 5%) the oil removal (Fig. 1). It was found (Northup and Cassidy, 2008) that as pH rises above the optimal, the amount of hydrogen peroxide released from calcium peroxide decreases rapidly making the chemical less effective for the modified-Fenton treatment. Thus, among the possible reasons of the oil removal retardation during a 1-d treatment with the highest (chemical/oil ratio of 0.3/1, w/w) dosage of calcium peroxide could be the hydrogen peroxide decomposition with the predominant production of oxygen instead of hydroxyl radicals observed (Arienzo, 2000; Northup and Cassidy, 2008) at the high pH values. Similar observations were performed for a 1-d treatment of soil with magnesium peroxide (Figs. 1 and 2).

Residual hydrogen peroxide was not found in soil both after 1 and 3 d of the treatment with lower dosages of calcium and magnesium peroxides (chemical/oil of 0.005/1, w/w) indicating the complete consumption of hydrogen peroxide. The highest concentration of the residual hydrogen peroxide in soil was found at the highest dosages (calcium peroxide or magnesium peroxide/oil of 0.3/1, w/w). Thus, the results on the residual hydrogen peroxide concentration in soil (Table 2) indicated that the formation of hydrogen peroxide could not be among the limiting factors of the oil removal at least during the application of the highest dosages of the chemicals. Consequently the variations in the dosages of either calcium peroxide or magnesium peroxide at the constant amount of the available natural activator in soil could influence the degradation of contaminant in soil by the creating different pH conditions. Since the degradation of contaminant could be limited by the ratio of hydrogen peroxide with an activator in an initial rapid degradation phase due to the non-productive decomposition of hydrogen peroxide at the pH values above or below the optimal.

The prolongation of the treatment time from 1 to 3 d at the lower dosages (chemical/oil ratios from 0.005/1 to 0.15/1, w/w) of the chemicals resulted in an unsubstantial increase in the oil removal (Fig. 1). While the application of a prolonged 3-d treatment at the highest ratios of the chemical/oil (calcium peroxide or magnesium peroxide/oil of 0.3/1, w/w) led to a nearly complete removal of the contaminant in soil. Increasing dosages of calcium and magnesium peroxides results (Arienzo, 2000; Northup and Cassidy, 2008) in increasing amount of $Ca(OH)_2$ and $Mg(OH)_2$ precipitation that could potentially limit PCBs extraction by their absorption onto the calcium hydroxide or magnesium hydroxide surface (Arienzo, 2000) and/or encapsulation of PCBs. For example, the addition of 1% of $Ca(OH)_2$ to the Aroclor 1016 contaminated soil in the study of Majid et al. (2002) resulted in 10% reduction of PCBs solubility in solvent and, as a result in some increase in the amount of unextractable PCBs residual. After the extraction the difference in Aroclor 1016 residual concentration in soil samples with and without 1% (w/w) of $Ca(OH)_2$ addition in the study of Majid et al. (2002) comprised 120 mg kg^{-1} of soil. In the present study the theoretical maximum amount of $Ca(OH)_2$ that could be formed in the reactions 1–2 during the soil treatment with the amount of added initially to the soil as a constitute of the calcium peroxide technical product was 1.3% (w/w). However, the difference in PCB residual concentrations measured in the samples neutralized by 10% phosphoric acid to 5.2 (the initial soil pH) and in the samples that were not pH adjusted was not evident. The results on the extractability reduction, due to much higher concentrations of Aroclor 1016 in soil, could fall within the standard deviation of the mean calculated based on the measurements of duplicates. Thus, the enhancement in the oil removal during the soil treatment by the highest calcium and magnesium peroxides dosages within prolonged (3 d) treatment time was probably achieved according to Arienzo (2000) due to a strong oxidative conditions created by a simultaneous generation of oxygen, hydrogen peroxide and calcium hydroxide.

In spite of nearly complete oil removal with a 3-d treatment was achieved, the application of such high dosages of the chemicals may be not reasonable, as more than 95% of the oil removal was achieved with the moderate calcium and magnesium peroxides additions (calcium peroxide or magnesium peroxide/oil of 0.005/1, w/w), but for a longer treatment time (21 d). As can be seen in Fig. 3, the increasing of the treatment time improved substantially the oil removal in soil. Therefore, in spite of the main advantage of either calcium peroxide or magnesium peroxide over the direct hydrogen peroxide application is the reduction in disproportionation of hydrogen peroxide consumption by the hydrogen peroxide auto-regulated release (Northup and Cassidy, 2008), still moderate dosages of calcium and magnesium peroxides and a prolonged treatment time could be recommended. In addition, only slight increase in the soil pH, from initial 5.2 to 5.8, for 21 d of the treatment with the moderate dosages of the chemicals was observed. While the substantial increase of the pH (Fig. 2) during the application of the highest dosages of calcium and magnesium

Table 2
Concentration of the residual hydrogen peroxide in 60% watered 1- and 3-d treated soil with either calcium peroxide or magnesium peroxide.

Treatment time, d	Concentration of the residual hydrogen peroxide in soil, µg residual H_2O_2 g^{-1} of soil					
	Calcium peroxide/oil, w/w			Magnesium peroxide/oil, w/w		
	0.005/1	0.05/1	0.3/1	0.005/1	0.05/1	0.3/1
1	0	0.68	14	0	0.08	1.4
3	0	0.94	5.0	0	0.04	2.1

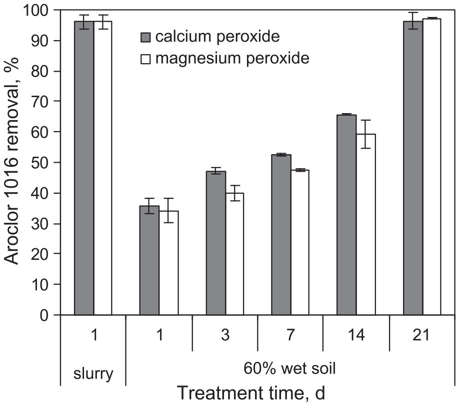

Fig. 3. Aroclor 1016 oil (initial concentration of 39 ± 1 g oil kg^{-1} of dry soil) removal (mean ± standard deviation) in soil slurry (treatment time 1 d) and in 60% watered soil (treatment time from 1 to 21 d) by either calcium peroxide or magnesium peroxide (chemical/oil of 0.005/1, w/w).

peroxides was noticed. Although strong buffering capacity of soil usually allowed restoring the initial pH during a certain period after the treatment, sudden variation in the pH can have a harmful effect on soil microbial community thereby retarding the following biodegradation of residual contaminants and/or their degradation by-products (Kao et al., 2001). The strong alkaline conditions (up to pH 12.5 depending on the chemical dosage) created during the 2,4,6-trinitrotoluene contaminated soil treatment with calcium peroxide were also observed by Arienzo (2000) who recommended lower calcium peroxide concentrations for soil treatment in order to sustain microbial activity.

The oil removal with calcium and magnesium peroxides was close (Figs. 1 and 3) at similar dosages of the chemicals applied independent of active compound, CaO_2 or MgO_2, content. The reason could be that the hydroxyl radical and/or other oxidative/reductive species production is dependent not only on the amount of hydrogen peroxide released from the chemical, but also on the activator/contaminant ratio that determines the hydroxyl radical/contaminant ratio in an initial rapid degradation phase (Pignatello et al., 2006).

The treatment of the soil in slurry under a vigorous magnetic-stirring with lower (calcium peroxide or magnesium peroxide/oil of 0.005/1, w/w) ratios of calcium peroxide or magnesium peroxide/oil led to nearly complete removal of the PCB-containing oil in soil for 1 d of the treatment (Fig. 3). Similar results were also obtained by Arienzo (2000), who found that the treatment of 2,4,6-trinitrotoluene contaminated soil in slurry with 0.2% (w/v) of calcium peroxide resulted in the complete removal of contaminant for 48 h. In the study of Northup and Cassidy (2008) nearly complete removal (99%) of polychlorethylene was achieved within 52–60 h of the soil slurry treatment with 0.2% (w/v) of calcium peroxide. A 1-d treatment of soil in slurry under a vigorous stirring resulted in more efficient oil removal than that of 60% watered soil (with the same dosages of the chemicals applied) probably due to the better desorption of the contaminant to the bulk solution. Pignatello et al. (2006) also suggested that the degradation of contaminants that undergo preliminary partitioning could be rate-limited by desorption, as the probability of hydroxyl radicals formed in the solution could encounter a sorbed molecule is extremely small. In addition, the rate of calcium and magnesium peroxides dissolution under a vigorous stirring might be considerably higher comparing with that achieved in once-pre-mixed slightly (60%) watered soil.

The pH of the soil slurry after 24 h of the treatment was slightly increased from initial 5.2 to 5.5, while the pH of unbuffered calcium peroxide and magnesium peroxide solutions (using similar dosages of the chemicals) in double-distilled water without the soil addition was 11 and 10, respectively. These results indicated a strong buffering capacity of the soil.

The yield of hydrogen peroxide during the dissolution of either calcium peroxide or magnesium peroxide in buffered (pH 5.5) double-distilled water without the soil addition under a vigorous stirring for 24 h was 295 mg H_2O_2 g^{-1} of calcium peroxide (82% of the theoretically possible) and 7 mg of H_2O_2 g^{-1} of magnesium peroxide (10% of the theoretically possible), respectively. However, the residual hydrogen peroxide was not found after a 1-d treatment of the soil in slurry indicating a complete decomposition of formed hydrogen peroxide.

Miserable (0.08 ± 0.01 mg Cl^- g^{-1} of oil removed, average for the treatment with both chemicals) chloride ion formation was observed in 60% watered soil treated with the moderate dosages of calcium and magnesium peroxides (calcium peroxide or magnesium peroxide/oil of 0.005/1, w/w). Chloride ion was not found in the study of Carberry and Yang (1994) on the PCB-contaminated soil treatment with hydrogen peroxide. It was suggested that the strong ionic strength of natural soil could entirely mask the actual production of chloride ion. Low (0.25 ± 0.01 mg Cl^- g^{-1} of oil removed) chloride ion formation was also observed during a 1-d treatment of oil contaminated soil with either calcium peroxide or magnesium peroxide in slurry.

3.2. DHA and microbial respiration in soil

In general, enzyme activity is an indicator of biological redox-systems that can be taken, as a measure for the intensity of microbial metabolism in soil (Schloter et al., 2003). DHA in soil slightly decreased after the addition of either calcium peroxide or magnesium peroxide in the present study (Table 3). However, after 3 d of incubation the DHA followed a similar pattern for the soil treated with either calcium peroxide or magnesium peroxide and for the soil without the peroxides addition. It was also shown by Arienzo (2000) that the treatment with low dosages of calcium peroxide (less than 0.2%) did not lead to the reduction in soil microbial phosphatase activity comparing with that in soil without the peroxides addition even after 7 d of the treatment.

Consumption of oxygen was measured in order to assess changes in the amount of soil microflora during the treatment with calcium and magnesium peroxides. The results showed that the oxygen consumption was not substantially changed for 21 d incubation with the application of calcium and magnesium peroxides (Table 3), indicating in a close metabolic activity of indigenous microbial populations in the soil treated with the peroxides and in the soil without the peroxides addition. Slight increase in the oxygen consumption corresponded to the changes in soil microbial

Table 3
DHA and oxygen consumption (mean ± standard deviation) in untreated soil and the soil treated with either calcium peroxide or magnesium peroxide (chemical/oil of 0.005/1, w/w).

Time, d	Untreated soil	Soil treated with CaO_2	Soil treated with MgO_2
	DHA, μg TPF h^{-1} g^{-1} of soil		
1	2.1 ± 0.0	1.5 ± 0.0	1.3 ± 0.1
3	1.7 ± 0.0	1.4 ± 0.1	1.3 ± 0.0
7	1.2 ± 0.1	1.4 ± 0.0	1.3 ± 0.1
14	1.3 ± 0.0	1.4 ± 0.2	1.5 ± 0.0
21	1.2 ± 0.0	1.2 ± 0.1	1.3 ± 0.1
	Oxygen consumption, μg O_2 h^{-1} g^{-1} of soil		
0–21	61 ± 5	70 ± 4	65 ± 6
22–28	69 ± 5	80 ± 4	73 ± 6

activity was observed after 21 d of incubation. Furthermore, the increase in oxygen consumption was more substantial in the peroxides treated soil than in the soil incubated without the peroxides addition. This enhancement in the activity of indigenous microorganisms of the peroxides treated soil was possibly achieved by oxygen release; increase of substrate solubility and improvement of nutrients availability to microbial cell.

In addition, the oxygen consumption observed during the treatment of the soil could be an indicator of organic contaminants aerobic biodegradation that possibly proceed along with the chemical oxidation of contaminants. Thus, it is difficult to make a distinction between the inputs of biological oxidation and chemical oxidation in contaminants removal during the prolonged treatment of soil with the solid peroxides. This is also supported by the study of Ndjou'ou et al. (2006), who have shown that the aerobic biodegradation co-exists with the modified-Fenton oxidation of contaminants in soil, even at the high dosages of hydroxyl radicals producing chemicals.

4. Conclusions

The oil removal efficacy in PCB-contaminated soil was found to be strongly dependent on dosage of the chemical, treatment time and treatment manner (the treatment of the vigorously mixed soil slurry or of the 60% watered, once-pre-mixed soil). PCB-containing electrical insulating oil removal with calcium peroxide and magnesium peroxide was close at the similar dosages of the chemicals independent of active compound, CaO_2 or MgO_2, content making a presumption that the amount of natural activators (transition metal ions and minerals) in treated soil influenced the degradation of the contaminant. The removal of PCB-containing electrical insulating oil was achieved with the addition of either calcium peroxide or magnesium peroxide alone and dependent on dosages of the chemicals due to pH conditions created. In spite of a 1-d treatment of soil in slurry under a vigorous stirring resulted in more efficient oil removal than that of 60% watered soil (with the same dosage of the chemical), such treatment manner is difficult to adopt for the practical application. Nearly complete (96 ± 2%) removal of oil and the unsubstantial increase in the soil pH was obtained by a 21-d treatment of 60% watered, once-pre-mixed soil with the moderate additions (chemical/oil of 0.005/1, w/w) of either calcium peroxide or magnesium peroxide. The results on the oxygen consumption and DHA indicated the unsubstantial changes in the amount of soil microflora and microbial activity by the moderate dosages (chemical/oil of 0.005/1, w/w) of both chemicals within 21 d of the treatment. Thus, a prolonged treatment time with the moderate addition of both chemicals could be recommended in order to reduce the non-productive hydrogen peroxide decomposition and to promote the coexistence of chemical and biological oxidation of contaminants.

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PAPER II

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Treatment of Aroclor 1016 contaminated soil by hydrogen peroxide: laboratory column study

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The potential and feasibility of treating soil contaminated with electrical insulating oil, Aroclor 1016, containing polychlorinated biphenyls (PCBs) with stabilized hydrogen peroxide were evaluated using columns packed with soils of two different matrixes. The column experiments showed that PCBs degraded by the stabilized hydrogen peroxide treatment in both soil matrixes, although the efficacy of the treatment depended strongly on the soil characteristics. The removal of PCB-containing oil was higher in sandy silt soil than in sandy soil. While a higher iron content promoted hydrogen peroxide oxidation of the contaminant in sandy silt soil, lower permeability and higher organic matter content contributed to an oxidation decrease as a function of depth. Dehydrogenase activity measurements indicated no substantial changes in microbial activity during the treatment of both sandy and sandy silt soils, thus offering opportunities to apply the hydrogen peroxide treatment to the remediation of PCB-contaminated soil.

Keywords: polychlorinated biphenyls; column experiments; oxidation; soil matrix; microbial activity

1. Introduction

Polychlorinated biphenyls (PCBs) are synthetic organic chemicals. There are 209 individual compounds. PCBs have been widely used as coolants and lubricants in transformers, capacitors, PVC plastics, paints, adhesives and other electrical equipment. PCBs have entered the environment since 1929 [1]. In spite of the production of PCBs being banned in the 1970s, they persist in the environment. In many circumstances, the environmental occurrence of PCBs has been associated with an adverse effect on public health. There is therefore a need to develop effective treatment methods for the degradation of PCBs.

Hydrogen peroxide is a powerful oxidizing agent, which can be delivered deep into the ground using lance permeation, soil mixing techniques or injected water amendments [2]. Chemical oxidation with hydrogen peroxide can be direct and/or involve generation of free radicals. Hydroxyl radicals ($OH^\bullet$), which are formed during the Fenton reaction (Equation (1)) [3] have traditionally been considered responsible for contaminant oxidation in all Fenton systems. However, Watts et al. [4] have shown that when high (≥2%) concentrations of H_2O_2 are used (the modified Fenton system), several reactions (Equations (2)–(4)) proceed beyond the first reaction:

$$H_2O_2 + Fe^{2+} \rightarrow OH^\bullet + OH^- + Fe^{3+} \quad (1)$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \quad (2)$$

$$HO_2^\bullet \rightarrow H^+ + O_2^{-\bullet} \quad pK_a = 4.8 \quad (3)$$

$$HO_2^\bullet + O_2^{-\bullet} \rightarrow HO_2^- + O_2 \quad (4)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \quad (5)$$

where $O_2^{-\bullet}$ is a superoxide radical anion, $HO_2^\bullet$ is the perhydroxyl radical and HO_2^- is the hydroperoxide anion. The perhydroxyl radical is a relatively weak oxidant; superoxide is a weak reductant and nucleophile, and the hydroperoxide anion is a strong nucleophile. This mixture of oxidants, reductants and nucleophiles can degrade almost all organic compounds. Moreover, many degradation products that are relatively unreactive with $OH^\bullet$ may be transformed by the reductants, which may enhance the potential for contaminant mineralization by the Fenton-like reactions [4]. However, the hydroxyl radical and/or other oxidative/reductive species production depends not only on amount of hydrogen peroxide added but also on the activator/contaminant ratio that determines the hydroxyl radical/contaminant ratio in an initial degradation phase [5].

In addition, low concentrations of hydrogen peroxide are usually used in the Fenton system to reduce the oxidation of ferrous iron to ferric iron. At the high (≥2%) hydrogen peroxide concentrations required to desorb contaminant, ferrous iron is rapidly oxidized to ferric iron, resulting in immediate consumption of the hydrogen peroxide (Equation (5)). Thus, it was found [6] that ferric iron is a more effective activator for the modified Fenton system because it does not result in un-productive decomposition of hydrogen peroxide and Equation (5) becomes negligible.

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While Fenton's reagent refers to iron-mediated hydroxyl production from H_2O_2 decomposition, hydrogen peroxide can be also decomposed by most ions of transition metals and by minerals of those metals [7]. Although other transition metals have not generally been found as efficient as iron in terms of their potential to create oxidizing conditions, they are very important for the hydrogen peroxide treatment of soil since natural soil may contain large quantities of these species. Thus, high concentrations of hydrogen peroxide can also be useful to facilitate desorption of natural soil activators to the bulk solution, where the reaction mainly proceeds. Because of their conservative nature and consistent rates of hydroxyl radical generation, heterogeneous mineral activators could be especially effective when high concentrations of hydrogen peroxide are used [4].

According to Watts et al. [8], the ability of minerals to promote the activation of hydrogen peroxide decomposition may occur at least by two mechanisms. The first is the activation of the hydrogen peroxide oxidation process through a mineral dissolution with release of soluble iron. At least three dissolution mechanisms of metal ions from natural soil minerals are distinguished [9], that is, protonation, complexation and reduction. The second mechanism is heterogeneous catalysis on mineral surfaces. A reaction mechanism in the mineral-catalysed modified Fenton system proposed by Miller and Valentine [10] incorporates a single rate-limiting step controlling H_2O_2 loss and ultimately contaminant degradation, superoxide and hydroxyl radical formation, scavenging reactions of oxygen radicals with the metal oxide sand surface, and contaminant degradation by reaction with hydroxyl radical which is formed from both surface and solution reactions.

The effect of the soil matrix on contaminant degradation efficacy by the hydrogen peroxide oxidation process is significant [11]. The soil matrix usually has an impact on the removal of the target compound with chemical oxidation as the organic and inorganic admixtures present in soil can compete for non-selective oxidants such as $OH^\bullet$ and, consequently, impede the elimination of pollutants. Several properties of soil such as heterogeneity, permeability, soil texture and humus content also substantially influence the applicability and effectiveness of the treatment. However, some additives such as soil natural minerals and soil transition metals non-chelated or chelated by natural chelating agents, organic substances (organic acids, amino acids and hydroxamate siderophores) either applied or produced by plants or microorganisms, may also act as activators and promoters, consequently, improving the process efficacy.

There are two studies on the treatment of PCB-contaminated soil and/or sediment by hydrogen peroxide in slurry. Carberry and Yang [12] found that a gradual addition of hydrogen peroxide and ferrous iron used as the activator substantially improved the degradation of PCBs in soil. Increased biodegradation of the contaminants after the soil treatment with hydrogen peroxide was observed. Aronstein and Rice [13] observed a substantial increase in the mineralization degree of 2-chlorobiphenyl in soil and sediment by the modified Fenton treatment compared with that achieved by the biological treatment alone. The by-products formed during the modified Fenton treatment were less hydrophobic than parent PCBs and therefore more available for further biodegradation [13]. Although the hydrogen peroxide treatment of PCB-contaminated soil in slurry was studied, column experiments can recreate oxidant flow dynamics and therefore it should be performed [14]. There were no studies on the hydrogen peroxide treatment of PCB-contaminated soil in columns in the literature. The effect of the soil matrix had also not been assessed.

Thus, the main objective of the present study was to evaluate the potential and feasibility of PCB-contaminated soil treatment with hydrogen peroxide using columns packed with a soil of higher iron content, organic carbon content and lower permeability and a soil of lower iron content, organic carbon content and higher permeability. The effect of the hydrogen peroxide on indigenous soil microorganisms, which it is known to be of great importance for estimation of the following biological treatment applicability [14], was also evaluated.

2. Materials and methods

2.1. Soil sample preparation and characterization

Natural topsoils (0–20 cm) were dried overnight at 30°C in a circulating air drying oven and sieved through a 2.0 mm sieve using a Retsch (AS 200 digit) sieve shaker before the spiking. The identification of the soil's texture was based on the principles established by ISO 14688-1,2 [15,16] using a laser scattering particle size distribution analyser (LA-950, Horiba). The textures of soils were identified as sandy silt and sand. Several characteristics of the soils are presented in Table 1.

Ferrous iron and ion-exchangeable Fe(II) fractions were extracted according to the procedure described by Tessier et al. [17]. Total extractable iron was extracted according to Heron et al. [18]. Iron in the extracts was measured photometrically by complex formation with

Table 1. Characteristics of untreated soils.

Property		
Soil texture	Sandy	Sandy silt
Sand (%)	99.5	45.5
Silt (%)	0.5	52
Glay (%)	0	2.5
pH	5.7	5.2
Ferrous iron fraction (g kg^{-1})	0	12.1 ± 0.9
Total extractable iron (mg kg^{-1})	11 ± 1.5	1900 ± 500
Ion-exchangeable Fe(II) fraction (mg kg^{-1})	0	2.0 ± 0.3
Organic carbon (mg kg^{-1})	44 ± 4	460 ± 30

1,10-phenanthrolinium chloride [19]. The organic carbon content of the soil was determined by sulfochromic oxidation [20]. Soil pH was measured according to method 9045C [21] using a digital pH meter (CG-840, Schott) equipped with a Mettler Toledo InLaB 412 electrode. Dehydrogenase activity (DHA) in the soil before and after the treatment was measured by triphenylformazan (TPF) production according to ISO/FDIS 23753-1 [22].

Electrical insulating oil, identified [23] as Aroclor 1016 – commercial formulation of light PCBs congers (12.9% of two-ring PCBs, 66.0% of three-ring PCBs, 21.0% of four-ring PCBs and 0.1% of five-ring PCBs), was obtained from an old capacitor. Soil was spiked with the oil ($55\,\mathrm{g\,kg^{-1}}$) under a continuous mixing for 5 h to ensure contaminant distribution homogeneity and hence better reproducibility in repeated experiments. The initial concentrations of the oil in the soil samples verified by the analysis of four replicates was $45.2 \pm 0.2\,\mathrm{g\,oil\,kg^{-1}}$ of dry sandy silt soil and $52.1 \pm 1.6\,\mathrm{g\,oil\,kg^{-1}}$ of dry sandy soil. PCB-containing oil recovery from the soils was 91% and 95% for the sandy silt soil and sandy soil, respectively.

2.2. *Soil treatment*

The column experiments were conducted using a 25-cm long section of nominal 8.5 cm diameter PVC pipe (Figure 1). The top of each column was constructed from PVC fittings tapped to accommodate Teflon (1.6 mm internal diameter, id) capillary tubes. The tube was closed at the end and perforated so that the hydrogen peroxide solution was spread sideways. A 6-cm tube was inserted into the soil. The column bottom was fitted with a Capron filter material. The columns were packed with 1 kg of either sandy soil or sandy silt soil to a density of 1.4 and $1.6\,\mathrm{g\,cm^{-3}}$ and a depth of 11.0 and 12.8 cm, respectively. Each column was operated in a batch upflow mode using a peristaltic pump (304, Salimp) to control the rate ($0.8\,\mathrm{mL\,s^{-1}}$) of inflow. The treatment was carried out by injecting 60 mL of 5.35 M H_2O_2 and 0.05 M KH_2PO_4 solution twice daily (6 h interval between the first and second injections, and 18 h between the second and third injections, etc.) for 10 days. The volume of H_2O_2 solution injected was selected in order to be sufficient to fully contact the soil. The total volume of H_2O_2 solution injected to the column was 1200 mL. The soil pH was not pre-adjusted. The columns were prepared in sets of two to provide duplicates. Samples from the column effluent were collected after each injection to measure the hydrogen peroxide residual concentration.

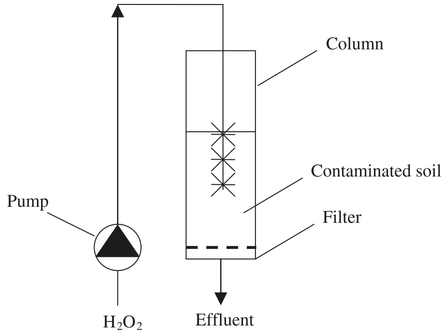

Figure 1. Schematic diagram of the column experiment on hydrogen peroxide treatment of contaminated soil.

The joint column effluent was analysed for the oil and anions (Cl^-, F^-, SO_4^{2-}, NO_3^-) content and chemical oxygen demand (COD). Residual hydrogen peroxide in the column effluent treated by titanium sulphate with pertitanic acid formation was measured photometrically at 410 nm [24]. Anions were detected using an ion chromatograph (761 Compact IC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm id) analytical column. COD was measured by the closed reflux, titrimetric method [25]. All experiments were carried out in duplicates at 20 ± 1°C. Results are presented with ± standard deviation of the mean ($n = 2$).

The treatment of the contaminated soil in slurry (10 g soil with 30 mL liquid) was carried out (without pH pre-adjustment) under vigorous (300 rpm) magnetic stirring in a closed cylindrical glass reactor with a 0.2 L of volume for 24 h. Different hydrogen peroxide/contaminant weight (w/w) ratios were applied.

2.3. *PCB-containing oil extraction and determination*

After a 10-day treatment of the soils, the columns were allowed to drain for 24 h and the column part packed with the soil dissected into three sections (section I: 0–3 cm; section II: 3.1–9.0 cm; section III: 9.1–11.0/12.8 cm sand/sandy silt from the top). Soil samples collected from each section in triplicate were dried with anhydrous sodium sulphate prior to extraction. Then dried soil sample was soaked in 10 mL of *n*-hexane (Rathburn, analytical grade) and placed for the extraction in a reciprocal shaker (358S, Elpan) overnight. A vortex (IKA, Genius3) extraction procedure was then used three times (10 mL of hexane each time) for three minutes each. Joined hexane extracts were mixed with internal standard (1/1). The internal standard was tridecane dissolved in *n*-hexane with a concentration of $3.3\,\mathrm{g\,L^{-1}}$.

The measurement of oil was carried out using a Focus GC, Finnigan GC-FID (Thermo Electron Corporation). Two microliters were injected splitless in a crossbond 100% dimethylpolysiloxane capillary column RTX®-1 (30.0 m × 320 μm id × 0.25 μm film thickness). The injector temperature was set to 200°C. The GC temperature programme started at 40°C, the initial temperature was held for 1 min then increased by $10°\mathrm{C\,min^{-1}}$ to 140°C, followed by $4°\mathrm{C\,min^{-1}}$ increased to 230°C; the final temperature was held for 2 min. The detector temperature was 200°C. The velocity of carrier gas (nitrogen) was 1 mL min^{-1}. The external standard was prepared by dissolving the PCB-containing oil used for the spiking in *n*-hexane. Quantification was based on the area count obtained for the merged peaks with peak start of 17 and peak end of 35 min. The detection limit of the method was 30 mg oil L^{-1} of hexane, which corresponds to 90 mg oil kg^{-1} of dry soil. The concentration of PCB-containing oil in soil was calculated on a dry weight basis. Dry matter in soil samples was determined by oven drying at 105°C. Gas chromatography- flame ionization detector (GC-FID) analyses of unspiked soil did not show any contaminant content.

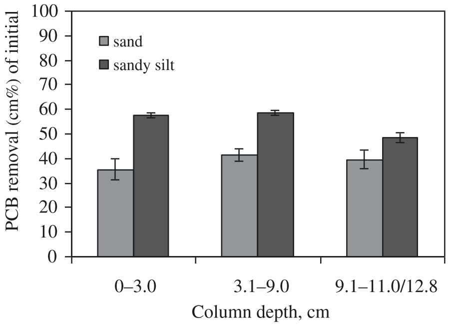

Figure 2. PCB-containing electrical insulating oil removal (% of initial, mean of column duplicates ± standard deviation) after the 10-day treatment of the sandy and sandy silt soils with hydrogen peroxide depending on column depth. The initial concentrations of PCB-containing electrical insulating oil were 45.2 ± 0.2 and 52.1 ± 1.6 g oil kg^{-1} of dry sandy silt soil and of sandy soil, respectively.

3. Results and discussion

Preliminary experiments on the treatment of sandy silt and sandy soils in slurry were conducted to identify the ability of hydrogen peroxide to oxidize PCBs without the addition of a supplemental activator. The removal of PCB-containing electrical insulating oil after a 24 h treatment of the soils in slurry was dependent on the dosage of hydrogen peroxide. A 2.5-fold upsurge in the hydrogen peroxide/oil weight ratio from 0.01/1 to 0.025/1 increased the oil removal level in sandy silt soil from 35.6 ± 2.6% to 69.5 ± 1.3%, respectively. Further increase in the hydrogen peroxide dosage (hydrogen peroxide/oil ratio increased from 0.025/1 to 2/1) resulted in an improvement in the degradation level leading to 73.3 ± 2.8% removal of PCB-containing oil in sandy silt soil within 24 h of the treatment. Similar observations were performed for sandy soil, where PCB removal increased within 24 h of the treatment with the increasing hydrogen peroxide dosage. Thus, the results of the present study showed that PCBs in both sandy and sandy silt soils could degrade with the addition of hydrogen peroxide only, indicating the possible ability of soil natural minerals or transition metals non-chelated or chelated by natural soil chelating agents to activate the hydrogen peroxide oxidation of PCBs at natural (Table 1) soil pH. The ability of naturally occurring transition metals and their minerals to activate the hydrogen peroxide oxidation of contaminants in soil [26–28] and in water [29–31] was also indicated in several studies.

The potential to apply hydrogen peroxide to the subsurface of contaminated soil was assessed using columns packed with a soil of higher iron, organic carbon content and lower permeability and a soil of lower iron, organic carbon content and higher permeability. The removal of the PCB-containing electrical insulating oil, Aroclor 1016, in sandy silt and sandy soils after a 10-day treatment with hydrogen peroxide in columns is shown in Figure 2. The stabilization of H_2O_2 with 50 mM KH_2PO_4 was performed to reduce the non-productive hydrogen peroxide decomposition during the contaminated soil treatment. It was found by Kakarla and Watts [32] that the increase in hydrogen peroxide migration was minimal at KH_2PO_4 concentration over 30 mM, considerably increasing the hexadecane decomposition with the reduced hydrogen peroxide consumption in the side reactions. Although phosphate may function as a radical scavenger due to quenching of hydroxyl radicals and terminating chain decomposition reactions [33], it also inhibits H_2O_2 decomposition [7] by lowering the concentrations of dissolved metals through either a precipitation reaction or, in the presence of excess phosphate, converting them to relatively stable complexes with the unanticipated rate of H_2O_2 decomposition providing additional contact time for the contaminant.

The efficacy of the removal of PCB-containing oil at the different depths of sandy soil was close (Figure 2). Oil removal in the sandy silt soil was similar at a depth of 0–9 cm and was somewhat reduced at the 9.1–12.8 cm depth. The permeability of sandy silt soil (0.003 cm s^{-1}) was much lower compared with that of sandy soil (0.0009 cm s^{-1}). Thus, the reduction in the removal level of the contaminant with the sandy silt soil depth was probably caused by the soil lower permeability resulting in the increased consumption of hydrogen peroxide in the upper layer, as lower permeability enables less even saturation of the soil with the remedial chemical. Although the short duration of H_2O_2 in the subsurface can prevent the diffusive transport of H_2O_2 into low permeable materials containing contaminants, higher contaminant removal efficacy in the upper layers of the soil contributes to the treatment of the PCB-contaminated soil by the liquid carrier of hydrogen peroxide on site. It is known that PCBs are hydrophobic contaminants that have a tendency to absorb in the upper layers of the soil [34].

The removal of Aroclor 1016 in the sandy soil was lower than that achieved in the sandy silt soil (Figure 2). Among the reasons for the lower oil removal in sandy soil compared to that in sandy silt soil could be the lower content of iron required for the productive decomposition of hydrogen peroxide. Non-productive reactions include the general disproportionation reaction (Equation (6)) where H_2O_2 is consumed and O_2 is a reaction by-product without production of $OH^{\bullet}$ [35].

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (6)$$

The treatment of the soils by hydrogen peroxide in columns resulted in a decrease in pH due to the acidic character of H_2O_2 solution injected. Some reduction in the soil pH can be caused by the acidic nature of hydrogen peroxide influencing the pH, especially at the high dosages of the chemical applied. These findings are in agreement with those of Gates-Anderson et al. [36], who observed a decrease in soil slurry pH after the addition of remedial chemical and indicated the ability of hydrogen peroxide treatment to remediate soils contaminated with trichloroethylene without pH pre-adjustment (at initial pH 8.7 and 5.7). In addition, the strong buffering capacity of soil usually allowed the initial pH during a certain period after the treatment. The bigger reduction in the pH obtained during the sandy silt soil treatment to 3.4 compared with that of 4.6 achieved during the sand treatment could be also caused by oxidation of sandy silt soil organic matter imposing the reduction in the buffering capacity.

The cumulative volume (472 ± 38 mL) of the sandy silt soil packed column joint effluent was lower than that of the sandy soil packed column (703 ± 14 mL). The volume is made up of 39 ± 3% and 59 ± 1% of the total volume (1200 mL) of the hydrogen peroxide solution injected to the sandy silt soil packed column and the sandy soil packed column, respectively. The lower soil permeability of the organic-rich sandy silt soil resulted in a higher liquid binding capacity compared with that obtained in sandy soil (Figure 3). Contrary to the treatment of sandy soil, where the column effluent (0.5 mL) was obtained after the first hydrogen peroxide injection, the first effluent (5 mL) from the sandy silt soil column appeared after six re-injections only.

Consumption of hydrogen peroxide during the sandy soil treatment was lower than that during the treatment of sandy silt soil; while 99.9% of injected hydrogen peroxide was decomposed during the sandy silt soil treatment, only 52.2 ± 1.4% was consumed during the sandy soil treatment. A wide range of naturally occurring reactants other than the target contaminant may also react with hydrogen peroxide imposing a background oxidant demand. Non-target reactants mainly include organic matter and reduced chemical species (ferrous iron, etc.). The background oxidant demand reduces oxidation efficacy and is generally greater than the demand imposed by the target compound. Thus, natural organic matter in the sandy silt soil could react with hydrogen peroxide, hydroxyl radicals and other oxidative/reductive species, known as non-selective oxidants [4], resulting in their consumption in the side reactions. Moreover, the reduction in hydrogen peroxide consumption (measured after each injection) in the sandy soil-packed column was observed along with an increase in the re-injection number (Figure 4). For example, while 80 ± 1% H_2O_2 was consumed during the first injection of the chemical to the sand, only 38 ± 2% of hydrogen peroxide consumption was obtained during the last injection. This can be attributed to the increased liquid content in the soil, which possibly resulted in less contact with metal oxide and organic matter reactants associated with the solid phase material. A near-complete (98–99.9%) consumption of hydrogen peroxide was obtained during each injection of the chemical to the sandy silt soil packed column.

Aroclor 1016 oil desorption to the liquid phase was observed within 10 days of the hydrogen peroxide treatment. PCB-containing oil concentrations (Table 2) found in the joint column effluent comprised 8.1% and 7.4% of the initial oil content in sandy and sandy silt soils, respectively. This should not create a problem during practical application as traps can be used to collect the effluent [37]. The treatment of the soils with hydrogen peroxide led to the desorption of the soils' anions to the bulk solution (Table 2), revealing the non-selective desorbing ability of

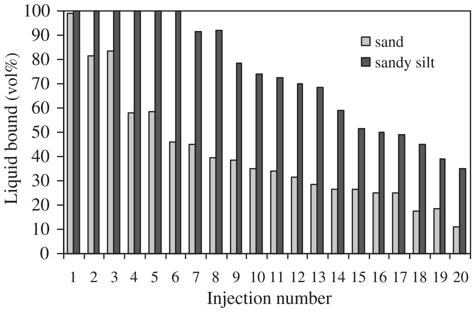

Figure 3. Liquid bound in the soil (vol.% of injected) after each injection (60 mL) of hydrogen peroxide to the sandy and sandy silt soils packed columns.

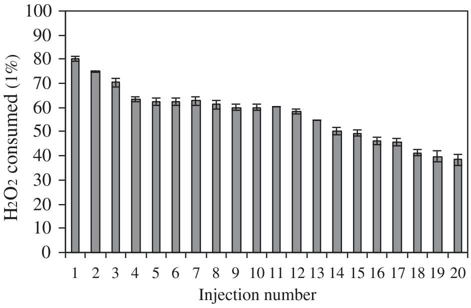

Figure 4. Hydrogen peroxide consumed (% of injected, mean of column duplicates ± standard deviation) during each injection to the sandy soil packed column.

Table 2. Properties of column joint effluent collected after 10-day treatment of the soils with hydrogen peroxide.

	Value, mean ± standard deviation	
Property	Sandy soil	Sandy silt soil
COD ($g\,O\,L^{-1}$)	<0.5	73.6 ± 1.1
Cl^- ($mg\,L^{-1}$)	24.5 ± 2.6	618 ± 31
F^- ($mg\,L^{-1}$)	10.8 ± 1.4	56.9 ± 1.1
NO_3^- ($mg\,L^{-1}$)	7.4 ± 0.1	17.2 ± 0.4
SO_4^{2-} ($mg\,L^{-1}$)	22.7 ± 0.1	185 ± 17
Concentration of the oil ($g\,L^{-1}$)	3.5 ± 0.2	2.8 ± 0.5

the chemical. The concentration of anions in the sandy silt soil-packed column effluent was higher than that in the effluent of the sandy soil-packed column.

The results obtained from the measurement of COD in the column joint effluent (Table 2) can be used as an indirect measure of mainly organic and some (susceptible to oxidation) inorganic compounds, and indicated a considerable release of natural organic matter to the bulk solution during hydrogen peroxide treatment of the soil. Chemical oxidation, by breaking down complex natural organic matter into simpler compounds with the formation of hydrophilic substances that are easier to degrade, can support the subsequent biodegradation of contaminants [38]. Moreover, the release of the organic matter to the bulk solution can also enhance the degradation of PCBs in the sandy silt soil. Kohl and Rice [39] found that at least 50% of bound PCBs could be associated with humin due to the strong adsorption capacity of organic carbon. Thus, release of humin to the bulk solution can account for PCB availability for the oxidation reaction, as it is known [10] that it mainly proceeds in the liquid phase.

The amount of DHA present (measured to assess changes in the amount of soil microflora and microbial activity) did not change during the treatment of both sandy and sandy silt soils (Figure 5). In general, enzyme activity is an indicator of biological redox systems that can be taken as a measure for the intensity of microbial metabolism in soil [40]. Thus, the effective removal of the PCB-containing oil with no changes in DHA makes hydrogen peroxide suitable for the treatment of both soil matrixes. Moreover, oxygen release (Equations (4) and (6)), possible increase of substrate solubility and nutrient availability to microbial cells during the application of hydrogen peroxide can potentially support the aerobic bioremediation of the PCB-contaminated soil by indigenous microorganisms.

There are several studies summarized by Sutton et al. [14] where the optimized hydrogen peroxide treatment of contaminated soil (various contaminants) was combined effectively with biological treatment. Studies by Carberry and Yang [12] and Aronstein and Rice [13] on the hydrogen peroxide treatment of PCB-contaminated soil in slurry also indicated a substantial enhancement in the subsequent biodegradation of the contaminants. Moreover, Ndjou'ou et al. [41] and Libisch et al. [42] found that the aerobic biodegradation of contaminants may even co-exist with the modified Fenton oxidation of contaminants in soil independent of high dosages of chemicals producing hydroxyl radicals. As a result, it could be difficult to draw a distinction between the inputs of biological oxidation and chemical oxidation in contaminant removal during the prolonged treatment of soil with hydrogen peroxide. Thus, a substantial difference in the DHA of the sandy soil and the sandy silt soil (Figure 5) could also be among the possible factors behind the differences in the removal efficacy of the contaminant (Figure 2). The higher DHA content of sandy silt soil compared with that of sandy soil could also result in the increased contaminant degradation. All these findings provide opportunities to apply combined oxidation with hydrogen peroxide and biodegradation for PCB-contaminated soil remediation.

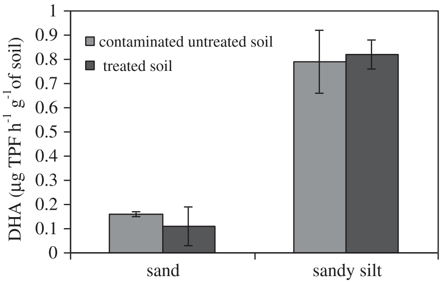

Figure 5. Dehydrogenase activity (DHA) in the contaminated untreated soil and the soil treated with hydrogen peroxide in columns (mean of column duplicates ± standard deviation).

4. Conclusions

The column experiments demonstrated that PCBs were degraded by the stabilized hydrogen peroxide treatment in both soil matrixes. However, the efficacy of the treatment was strongly dependent on the soil characteristics. The degradation of PCBs in sandy silt soil was higher than that in sandy soil. In spite of lower permeability, the higher iron content of sandy silt soil could promote hydrogen peroxide oxidation of the contaminants. The higher DHA content of the sandy silt soil could also probably improve degradation efficacy. While the efficacy of the PCB-containing oil removal decreased with sandy silt soil depth, the removal of the oil in the sand-packed column was even in all the soil layers studied. Thus, the lower permeability and higher organic matter content of the sandy silt soil may contribute to the oxidation decrease as a function of depth. Increased consumption of hydrogen peroxide and amount of liquid bound in the soil, as well as a substantial release of natural soil anions and organic matter (measured as COD) to the bulk solution, were observed during the sandy silt soil treatment. The decrease in pH was also somewhat higher in the sandy silt soil than that obtained during the treatment of the sandy soil. The DHA measurements indicated no substantial changes in the amount of soil microflora and microbial activity during the treatment of both sandy and sandy silt soils, providing opportunities to apply combined oxidation with hydrogen peroxide (as a mass removal step) and biodegradation (as a polishing step) for PCB-contaminated soil remediation.

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PAPER III

Goi, A., Viisimaa, M., Karpenko, O. (2012). DDT-contaminated soil treatment with persulfate and hydrogen peroxide utilizing different activation aids and the chemicals combination with biosurfactant. – *Journal of Advanced Oxidation Technologies*, 15(1), 41-52.

DDT-Contaminated Soil Treatment with Persulfate and Hydrogen Peroxide Utilizing Different Activation Aids and the Chemicals Combination with Biosurfactant

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Abstract:

The efficacy of DDT-contaminated soil treatment with hydrogen peroxide and persulfate utilizing different activation aids and the chemicals combination with biosurfactant was evaluated. The addition of a supplementary activator was able to improve the degradation of total DDT with both the hydrogen peroxide and persulfate oxidation processes indicating a lack of available activator. Ferrous iron added gradually was effectively utilized in the oxidation system with gradual addition of hydrogen peroxide, while chelated metal iron addition promoted the oxidation with more stable persulfate. The treatment with solid carriers of hydrogen peroxide, either calcium peroxide or magnesium peroxide, can be an effective alternative to the liquid one resulting in a higher degradation level of the contaminant. Strong alkalization with elevated dosages of NaOH sustained the persulfate oxidation of DDT. The addition of biosurfactant, rhamnolipid-alginate complex obtained by biosynthesis of strain *Pseudomonas* sp. PS-17, and EDTA improved the degradation of DDT by both persulfate and hydrogen peroxide oxidation processes indicating that the combined application of chemical oxidants and biosurfactant at natural soil pH has prospects as an effective option for contaminated soil remediation.

Keywords: soil decontamination; biosurfactant; chelated iron; hydrogen peroxide solid carrier; base activated persulfate

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Introduction

DDT (2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane) is the key compound in the group of the organochlorine pesticides, which proved to have detrimental environmental effect and concern as persistent toxic pollutant. DDE (2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene) and DDD (2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane) exist as impurities in technical-grade DDT formulations and form as a result of the abiotic transformation, aerobic biotic degradation and photochemical decomposition of DDT (1). The combined concentration of DDT and its metabolites in a sample is generally denoted as total DDT (2). In spite of the reduction in the production and use accompanied by bans and other restrictions, DDT remains widely dispersed in the environment. It happens due to long-range atmospheric transport processes, sea currents and local "hot spots". Moreover, DDT low solubility and bioavailability resist the application of many conventional treatment methods for its degradation.

Chemical oxidation is an innovative technology of degrading an extensive variety of hazardous compounds for the treatment of soil at waste disposal and spill sites. Among the chemicals, hydrogen peroxide is one of the most extensively used for the treatment of contaminated soil (3). Another promising approach could be combined application of biosurfactants and chemical oxidants. There are several studies (4-6), where synthetic surfactants of Triton X group were used in order to enhance the degradation of DDT and its metabolites (DDD, DDE) in water and soil by the treatment methods mostly utilizing zero-valent iron. In spite of the surfactants ability to improve substantial the DDT solubility, some of synthetic surfactants (or their degradation by-products) could become potential contaminants in surface and groundwater. The application of biosurfactants that are biologically produced by bacteria or yeast from various substrates including sugars, oil alkanes and wastes (7) can be even more effective due to their apparent advantages over the extensively used synthetic surfactants including high specificity, biodegradability and biocompatibility (8).

Previously, it has been found (9) that the addition of biosurfactant and acetone could enhance DDT, DDD and DDE release to bulk solution facilitating the dechlorination of the contaminants in soil slurry with magnesium/palladium system. Thus, biosurfactants

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*Corresponding author; E-mail address: Anna.Goi@ttu.ee may also potentially act as stimulators of the chemical oxidation processes, increasing contaminants availability to oxidizing agents as the oxidation processes mainly occur (10) in liquid phase.

DDT-contaminated soil washing with non-ionic synthetic surfactant Triton X-100 with the following separation of the liquid phase and its treatment by the photo-Fenton was found (11) to be effective for the soil decontamination. However, reports evaluating the potential of the combined application of chemical oxidants and biosurfactants that due to their biodegradability, low toxicity and high efficiency in various conditions can substitute their synthetic counterparts in the environmental applications have not been published to date. Moreover, if simultaneous application of biosurfactants and chemical oxidants without solid-liquid separation will be effective, then such a process modification would provide the treatment cost reduction and the increase of the subsurface treatment efficacy.

Proper selection of the remedial chemical and the activation aid is also of a great importance for the effective oxidation of contaminants in soil. Few studies (12, 13) have evaluated the potential of the activated hydrogen peroxide oxidation process applied for DDT-contaminated soil remediation. They demonstrated the efficacy of DDT-contaminated soil treatment with the hydrogen peroxide oxidation process activated by supplementary ferrous iron. However, the requirement for acidic conditions needed to keep iron soluble limits the utility of ferrous iron to activate the hydrogen peroxide oxidation for contaminated soil remediation at natural soil pH that lies usually in the range of 4-8 (14). A chelation of natural metal ions of soil can promote the chemical oxidation of contaminants in a wider pH range. Thus, the potential and efficacy of the hydrogen peroxide oxidation process activated by a chelated iron in DDT-contaminated soil treatment should be evaluated.

In addition, there are no published studies on DDT-contaminated soil treatment with solid carries of hydrogen peroxide such as calcium and magnesium peroxides. The treatment process utilizes liquid carrier of hydrogen peroxide has several disadvantages such as violent exothermic reaction and a rapid consumption of the oxidant. These disadvantages were also emphasized in the study of Villa et al. (13) on the hydrogen peroxide treatment of DDT-contaminated soil. The application of the solid carriers of hydrogen peroxide that have a benefit of slow hydrogen peroxide release (15) achieved during their contact with percolation water of soil can solve the mentioned drawbacks. Persulfate, another newest chemical oxidant recently received attention due to its increased stability in the subsurface (16) should also be considered as an alternative to hydrogen peroxide for DDT-contaminated soil treatment.

Therefore, the main goals of the present study were 1) to evaluate and compare the individual chemical (persulfate, liquid carrier of hydrogen peroxide and solid carriers of hydrogen peroxide - calcium peroxide and magnesium peroxide) impact on DDT-contaminated soil treatment; 2) to test different activation aids (supplemental application of non-chelated/chelated ferrous and ferric iron, chelation of natural transition metals of soil, base activation of persulfate, combined application of persulfate and hydrogen peroxide, application of acidic pH conditions to sustain the persulfate and hydrogen peroxide activation processes) as the application of that depends not only on the remedial chemical used, but also on the target contaminant; and 3) to resolve the benefits of the combined treatment with biosurfactant, rhamnolipid-alginate complex obtained by biosynthesis of strain *Pseudomonas* sp. PS-17, and the chemicals.

Experimental and Methods

Soil Sample Preparation and Characterization

Natural topsoil (0-20 cm) was dried over-night at 30 °C in a circulating air-drying oven before the spiking and sieved through a 30 mm sieve using a Retsch (AS 200) digital sieve shaker. Several characteristics of the soil are presented in Table 1. Ferrous iron and ion-exchangeable Fe(II) fractions were extracted according to the procedure presented by Tessier et al. (17). Total extractable iron of the soil was extracted according to Heron et al. (18). Iron in the extracts was measured photometrically at 492 nm with phenanthroline method (19). Soil pH was measured according to EPA method 9045C (20) using a digital pH meter (CG-840, Schott) equipped with a Mettler Toledo InLaB 412 electrode. Organic carbon of the soil was determined by sulfochromic oxidation (21). The identification of soil texture was based on the principles established by ISO 14688-1,2 (22, 23) using a laser scattering particle size distribution analyzer (LA-950, Horiba). The texture of the soil was identified as the sandy silt.

Soil Contaminant

Dry soil was spiked with a commercial preparation of organochloride pesticide DDT (1 g of product contained 0.273 g of total DDT: 0.187, 0.058 and 0.028 g of DDT, DDD and DDE, respectively) by adding contaminant-acetone solution. Acetone, purchased from Rathburn, was evaporated to dryness under a continuous mixing to ensure the contaminant

Table 1. Several characteristics of the untreated soil.

Parameter, unit	**Value (mean ± standard deviation)**
pH	5.88
Ferrous iron fraction (g kg^{-1} of soil)	1.9 ± 0.5
Total extractable iron (g kg^{-1} of soil)	12.1 ± 0.9
Ion-exchangeable Fe(II) fraction (mg kg^{-1} of soil)	2.0 ± 0.3
Organic carbon (mg kg^{-1} of soil)	460 ± 30
Sand (%)	45.5
Silt (%)	52
Clay (%)	2.5

distribution homogeneity and, hence, a better reproducibility in repeated experiments. The contamination was aged for 120 d. Combine concentration of DDT and its metabolites (DDD and DDE), denoted as total DDT concentration, was found to be 1.719 ± 0.288 g kg^{-1} of soil. The initial concentrations of DDT, DDD and DDE, verified by the analysis of eleven replicates, were 1.159 ± 0.207, 0.423 ± 0.103, 0.137 ± 0.059 g kg^{-1} of dry soil, respectively. Contaminants recovery was 87 ± 14%.

Soil Treatment

Biosurfactant solution (pH of 7) was added in different concentrations to the soil (solid/liquid ratio of 1/2, w/v) 24 h prior the chemicals addition. No mixing was applied within the following 24 h. The biosurfactant was rhamnolipid-alginate complex obtained (24, 25) by biosynthesis of strain *Pseudomonas* sp. PS-17 (the collection of microorganisms of the Department of Physicochemistry of Combustive Minerals of L.M. Litvinenko Institute of Physical-Organic and Coal Chemistry of the National Academy of Sciences of Ukraine). The complex was isolated from cultural liquid via acidic precipitation in form of 50% concentrate.

Sodium peroxodisulfate ($Na_2S_2O_8$, min 99%), purchased from Riedel-de Haën, calcium peroxide (CaO_2 and $Ca(OH)_2$ mixture, powder, 200 mesh (0.075 mm), commercially available product) and magnesium peroxide (MgO_2 and MgO mixture, powder, 100 mesh (0.152 mm) with 50% min through 200 mesh (0.075 mm), commercially available product), purchased from Aldrich, and hydrogen peroxide (35%), purchased from Sigma-Aldrich, were used as the remedial chemicals. The measured (15) contents of CaO_2 in calcium peroxide and MgO_2 in magnesium peroxide products were 76.4 ± 0.1% (with 17.0 ± 0.1% w/w of available oxygen) and 11.6 ± 0.1% (with 3.3 ± 0.1% w/w of available oxygen), respectively.

The $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 2H_2O$ salts, purchased from Sigma-Aldrich, were used as supplementary activator sources. Ferrous iron chelated with EDTA for the activation of the hydrogen peroxide or persulfate oxidation of DDT in soil was also tested. A stock solution of Fe(II)-EDTA with chelate/Fe^{2+} weight ratio of 1/5 was prepared by first dissolving of EDTA with EDTA disodium salt/EDTA tetrasodium salt weight ratio of 2/1 and then of ferrous sulfate. The appropriate volume of the stock solution was added to the slurry achieving the desired dose. For the chelating of natural activators present in soil, EDTA (EDTA disodium salt/EDTA tetrasodium salt weight ratio of 2/1) solution (stock solution with the concentration of EDTA 0.1 g L^{-1}) utilizing the same dose as in the experiments with Fe^{2+}-EDTA complex was added 30 min prior the application of the oxidizing chemicals.

The examination of pH effect was carried out by adjusting of soil slurry pH with H_2SO_4 or NaOH.

The chemical treatment of DDT-contaminated soil in slurry was carried out with different soil/chemical weight ratios (w/w) in a batch mode. The standard procedure was that slurry of 10 g soil with 30 mL liquid (biosurfactant solution and/or bi-distilled water and solutions of the chemicals) was treated in the cylindrical glass reactor with a 0.2-L of volume under a vigorous (300 rpm) magnetic-stirring during 24 h. In the experiments on the metal ion activated persulfate or hydrogen peroxide oxidation of DDT, activator (ferrous iron, ferric iron or chelated ferrous iron) solution was first added all at once or gradually (2 additions: 0, 4 h) and then the reaction was initiated by single or gradual (2 additions: 0, 4 h) addition of the chemicals solution.

In the experiments on the treatment of 60%-watered soil with calcium and magnesium peroxides, 10 g of moist (with 60% of double-distilled, autoclaved water) soil were mixed with the calcium peroxide or magnesium peroxide technical products (powder) and then treated without the pH pre-adjustment and stirring in the cylindrical glass reactor with a 0.2-L of volume for 24 h.

The flasks were sealed with a laboratory film (Parafilm) to reduce volatilization losses. All experiments were carried out in duplicates at 20 ± 1 °C. Results are presented with ± standard deviation of the mean.

Chemical Analysis

After the treatment, the solid phase was settled for 30 min and the supernatant was separated and filtrated (paper filter, Filtrak 160). The solid phase was dried with anhydrous Na_2SO_4, obtained from Lach-Ner. Dried soil with the filter was soaked in 10 mL of n-hexane/acetone (1/1, v/v) and placed for the extraction to a laboratory reciprocal shaker (358S, Elpan) overnight. Then, a vortex (IKA, Genius3) extraction procedure three times (30 mL of n-hexane/acetone of 1/1 v/v each time) per 2 min was used. Joined extracts were evaporated dry and the residue was dissolved in 1 mL of acetone and 1 mL of n-hexane with internal standard. The internal standard was hexadecane dissolved in n-hexane with the concentration of 0.2 g L^{-1}. Similar extraction procedure was applied for the initial untreated soil. The liquid phase separated after the soil treatment was vortex extracted with two portions of n-hexane/acetone (1/1, v/v) for 2 min. Joined extracts were mixed (1/1, v/v) with the internal standard.

The measurement of total DDT (DDT and its metabolites - DDD, DDE) was carried out using a FocusGC, Finnigan GC-FID (Thermo Electron Corporation). 2 μL were injected splitless in a cross-bond 100% dimethylpolysiloxane capillary column RTX-1 (30 m x 320 μm id x 0.25 μm film thickness). The injector temperature was set to 230 °C. The GC temperature program started at 40 °C, the initial temperature was held for 1 min then increased by 10 °C min^{-1} to 270 °C, and held for 3 min. The detector temperature was 330 °C. The velocity of carrier gas (nitrogen) was 1 mL min^{-1}. External standard was prepared by dissolving DDT, DDD, DDE standards (99% purity, Supelco) in a mixture (1/1, v/v) of n-hexane and acetone. The detection limit of the method was 20.6 mg DDE, 23.6 mg DDD and 26.2 mg DDT L^{-1} of solvent that corresponds to 4.1 mg DDE, 4.7 mg DDD and 5.2 mg DDT kg^{-1} of dry soil. Contaminants concentration in soil was calculated per dry weight. The GC-FID analyses of un-spiked soil did not show any content of contaminants.

Residual hydrogen peroxide in the supernatant treated by titanium sulfate with pertitanic acid formation was measured photometrically at 410 nm (26). Residual persulfate was detected photometrically (Heλios UV-vis spectrophotometer, Thermo Electron Corporation) at 446 nm as *o*-dianisidine-peroxydisulfate complex (27). pH after the treatment was measured using a digital pH meter (CG-840, Schott) equipped with a Mettler Toledo InLaB 412 electrode.

Residual ferrous iron concentration in the supernatant was measured photometrically (Heλios UV-vis spectrophotometer, Thermo Electron Corporation) at 492 nm by means of 1,10-phenanthrolinium chloride (19).

Results and Discussion

Persulfate and/or Hydrogen Peroxide Oxidation of DDT

The results of the present study showed (Figure 1) that total DDT (DDT, DDD, DDE mixture) in soil could degrade to some level (33 ± 2% of total DDT residual) with the addition of hydrogen peroxide only indicating a possible ability of soil natural minerals or transition metals chelated by natural soil chelating agents, (such as organic acids, amino acids and hydroxamate siderophores of soil) either applied or produced by plants or microorganisms, to activate the hydrogen peroxide oxidation of DDT at natural (Table 1) soil pH. A potential of naturally occurring minerals and transition metals of soil to activate the hydrogen peroxide oxidation was indicated in several studies (28-31) and the reaction mechanism in mineral-catalyzed Fenton system was proposed (32).

DDT could also degrade with the addition of persulfate only (Figure 1). It is known (33) that the persulfate decomposition is extremely sensitive even to the traces of metal ions. In spite of in the study of Ahmad et al. (34) was found that soil minerals did not promote the generation of oxidants and reductants during the persulfate decomposition, the degradation of contaminants in soil by persulfate addition alone was also observed in the other studies (35).

The degradation of total DDT in soil with either hydrogen peroxide or persulfate was uncompleted and independent of the chemicals dosages used, resulting in the same level of DDT removal (Figure 1). After a 24-h treatment with persulfate the DDT removal was slightly (by 5%) higher than that with hydrogen peroxide applying similar dosages of the chemicals (Figure 1). While hydrogen peroxide was completely decomposed during a 24-h treatment independent of the dosage used, the persulfate was found to be more stable. 37, 67, 75 and 79% of the initially applied persulfate remained after a 24-h treatment of soil with the weight ratios of soil/persulfate of 1/0.00012, 1/0.0012, 1/0.0024 and 1/0.0037, respectively. Consumption of persulfate, calculated in g of persulfate

Table 2. pH after a 24-h treatment with persulfate and hydrogen peroxide.

Soil/chemical/Fe^{2+}, w/w/w	**pH after the treatment with persulfate**	**pH after the treatment with hydrogen peroxide**
1/0.0006/0	5.62	6.45
1/0.0012/0	5.54	6.70
1/0.0024/0	5.25	6.80
1/0.0037/0	5.18	6.89
1/0.0012/0.00012	5.25	6.19
1/0.0012/0.00024	4.74	5.25
1/(0.0006 + 0.0006)/(0.00012 + 0.00012)	5.45	5.42
1/0.0006/0, initial pH of 3.5	4.13	3.79
1/0.0012/0, initial pH of 3.5	4.31	4.25
1/0.0024/0, initial pH of 3.5	4.58	4.27

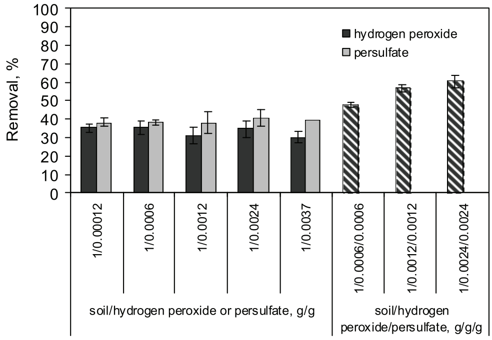

Figure 1. Total DDT removal (% of initial, mean ± standard deviation) after a 24-h treatment of soil at natural soil pH with hydrogen peroxide and/or persulfate at different weight ratios of soil/chemical.

decomposed per g of DDT degraded, increased with the ratios of soil/persulfate applied. For example, 0.12, 0.63, 0.90 and 1.1 g of $S_2O_8^{2-}$ were consumed per g of DDT degraded within 24 h of the treatment at soil/persulfate ratios of 1/0.00012, 1/0.0012, 1/0.0024 and 1/0.0037, respectively. The loss of the chemicals without the degradation of the contaminant could be explained by the competing reactions (3, 33, 36) such as non-productive chemicals decomposition without the generation of oxidants, reaction with the soil organic matter and reduced minerals, etc. Thus, the increased consumption of persulfate and hydrogen peroxide at equal level of DDT removal makes no sense in application of elevated loads of the chemicals.

The changes in the soil pH were not substantial during the treatment with persulfate (Table 2). Even the application of the highest dosage of persulfate (soil/persulfate of 1/0.0037, g/g) resulted in only slight pH drop from initial 5.88 to 5.18 within 24 h of the treatment. It was emphasized in the study of Liang et al. (37) on the persulfate treatment of trichloroethylene-contaminated soil that soil buffering capacity usually appeared sufficient to offer resistance to pH changes during the persulfate decomposition. In contrast to the persulfate treatment, a substantial increase in the pH with the increasing of the hydrogen peroxide dosage was observed (Table 2).

The treatment of soil with a dual chemicals system utilizing both hydrogen peroxide and persulfate resulted in a higher total DDT degradation level compared to that obtained by the treatment with a single chemical application (Figure 1). It was hypothesized (38) that the combined usage of hydrogen peroxide and persulfate may provide a multi-radical attack mechanism, yielding a higher efficacy in destroying contaminants, or allowing recalcitrant compounds to be more readily degraded. A possible reaction mechanism was presented in the study of Tsao and Wilmarth (39). It was suggested that hydroxyl radicals can initiate sulfate radicals formation, while sulfate radicals can stimulate production of hydroxyl radicals (Eqs. 1-5).

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} \tag{1}$$

$$SO_4^{-\bullet} + H_2O \rightarrow H^+ + SO_4^{2-} + OH^\bullet \tag{2}$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{3}$$

$$HO_2^\bullet + S_2O_8^{2-} \rightarrow O_2 + HSO_4^- + SO_4^{2-} \tag{4}$$

$$HO_2^\bullet + H_2O_2 \rightarrow O_2 + H_2O + OH^\bullet \tag{5}$$

A two-fold increase of $H_2O_2/S_2O_8^{2-}$/soil weight ratio from 0.0006/0.0006/1 to 0.0012/0.0012/1 slightly (by 9%) improved the degradation of total DDT. No effect of higher $H_2O_2/S_2O_8^{2-}$/soil = 0.0024/0.0024/1 weight ratio application on the DDT degradation was observed. Near-complete (99%) decomposition of hydrogen peroxide was achieved within a 24-h treatment at all the ratios of chemicals applied. In addition, 91% (0.12 g of persulfate consumed per g of DDT degraded) and 93% (0.17 g of persulfate consumed per g of DDT degraded) of initially applied persulfate were decomposed within a 24-h treatment at the H_2O_2/$S_2O_8^{2-}$/soil ratios of 0.0012/0.0012/1 and 0.0024/0.0024/1, respectively. Thus, lower ratios of H_2O_2/$S_2O_8^{2-}$/soil should be applied in order to avoid competing reactions (36) of hydrogen peroxide and persulfate with oxidizing agents instead of target contaminant. Some decrease in the pH after a 24-h treatment with the increase of both, hydrogen peroxide and persulfate dosages was observed. The pH values of 5.28, 5.18 and 4.96 were obtained after a 24-h treatment at the soil/H_2O_2/$S_2O_8^{2-}$ ratios of 1/0.0006/0.0006, 1/0.0012/0.0012 and 1/0.0024/0.0024, respectively.

The application of hydrogen peroxide solid carriers, either calcium peroxide or magnesium peroxide, known as the sources of hydrogen peroxide produced during their decomposition in contact with water (15, 40, 41) resulted in higher DDT removal level comparing with that achieved by the usage of the liquid carrier of hydrogen peroxide. As can be seen in Figures 1 and 2, the application of similar dosages of hydrogen peroxide and calcium peroxide (soil/chemical of 1/0.0006, g/g) for the soil treatment in slurry resulted in 35% and 83% of total DDT removal, respectively. It is known (41) that the main advantage of the solid carrier of hydrogen peroxide over the liquid one is the ability to release H_2O_2 slowly that reduces its non-productive decomposition usually observed (32) during a non-supplemented direct hydrogen peroxide application. Thus, the hydrogen peroxide solid carriers (calcium and magnesium peroxides) can be used as effective alternatives to the liquid one for DDT-contaminated soil treatment.

However, the degradation of total DDT was close (Figure 2) at equal dosages of calcium peroxide and magnesium peroxide (technical product) independent of the active compound, CaO_2 and MgO_2, content. Moreover, similar to the treatment with hydrogen peroxide or persulfate, the increase in the calcium peroxide and magnesium peroxide dosages (the weight ratio of soil/chemical decreased from 1/0.00016 to 1/0.0006) did not enhance the degradation resulting in the same level of contaminant removal. The difference in the pH, that found (15, 41) to have influence on the treatment efficacy with solid carriers of hydrogen peroxide, was insignificant after a 24-h treatment with similar dosages of the chemicals. The pH values were 6.8 and 6.9 after a 24-h slurry treatment at the soil/chemical ratio of 1/0.00016 with magnesium peroxide and calcium peroxide, respectively. The increase of the soil/chemical ratio to 1/0.0006 resulted in the pH of 7.4 and 7.2 for the soil treated with calcium peroxide and magnesium peroxide, respectively. Thus, slight variations in the pH created (40) by the difference in concentrations of both $Ca(OH)_2$ or $Mg(OH)_2$ released and CaO_2 or MgO_2 loaded, did not influence the efficacy of the treatment of DDT-contaminated soil. However, a mode of the treatment (the treatment of soil in slurry under a vigorous magnetic stirring or the treatment of once pre-mixed 60%-watered soil) considerably affected the treatment efficacy. A 24-h treatment of soil in slurry with the hydrogen peroxide solid carriers resulted in a higher degradation level of DDT than that obtained by the treatment of 60%-watered soil. This difference was probably achieved by better desorption of the contaminant and/or natural activator to the bulk solution and increased dissolution rate of calcium and magnesium peroxides under vigorous mixing conditions in slurry. The influence of the hydrogen peroxide solid carrier dissolution rate on contaminants degradation was also observed in the studies of Goi et al. (15) and Xu et al. (42).

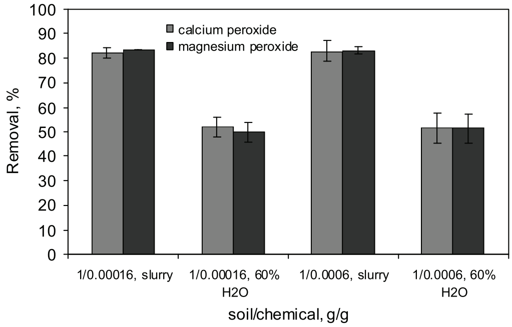

Figure 2. Total DDT removal (% of initial, mean ± standard deviation) after a 24-h treatment of soil at natural soil pH in slurry and of 60%-watered soil with calcium peroxide or magnesium peroxide at different weight ratios of soil/chemical.

Hydrogen Peroxide and Persulfate Oxidation of DDT Utilizing Supplementary Iron and/or EDTA

Higher degradation level of total DDT was achieved with addition of supplementary ferrous iron than that obtained by persulfate or hydrogen peroxide addition alone (Figures 3 and 4) suggesting a lack of available activator, but not the oxidant. For example, a DDT degradation level obtained by the treatment with non-supplemented persulfate application (soil/$S_2O_8^{2-}$ of 1/0.0006) was by 11% lower than that obtained by the treatment with the persulfate oxidation activated by supplementary ferrous iron ($S_2O_8^{2-}$/Fe^{2+} of 1/0.1) (Figure 3). It should be noted that the consumption of non-supplemented persulfate within 24 h of the treatment was nearly twice as high as that of persulfate activated by supplementary ferrous iron (Figure 5).

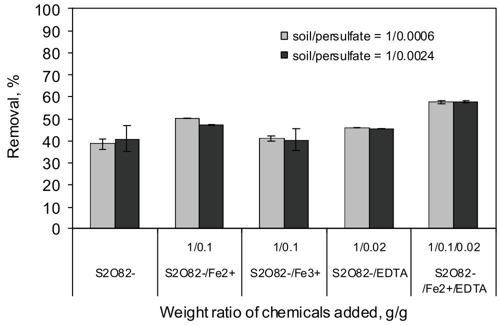

Figure 3. Total DDT removal (% of initial, mean ± standard deviation) by a 24-h treatment of soil at natural soil pH with persulfate applying ferrous iron, ferric iron, EDTA chelated ferrous iron and EDTA only.

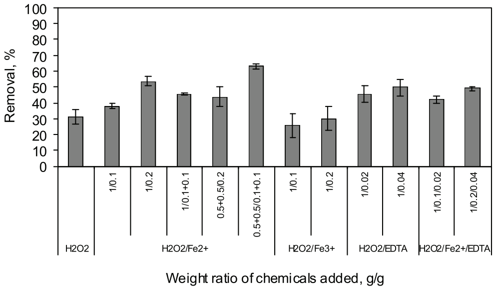

Figure 4. Total DDT removal (% of initial, mean ± standard deviation) by a 24-h treatment of soil at natural soil pH with hydrogen peroxide (soil/hydrogen peroxide of 1/0.0012, g/g) applying ferrous iron, ferric iron, EDTA chelated ferrous iron and EDTA only.

However, a double increase in supplementary ferrous iron dosage (the ratio of persulfate/ferrous iron changed from 1/0.1 to 1/0.2) not only reduced the degradation of the contaminant, but also resulted in a complete consumption of persulfate. Although gradual addition of both persulfate and the activator during the treatment with persulfate/ferrous iron of 1/0.2 allowed reducing consumption of persulfate to 69% the degradation of DDT was not increased (Figure 5). Thus, an excess in ferrous iron concentration can diminish contaminant degradation efficacy during the persulfate oxidation process. Similar observations were performed by Liang et al. (43) in the study on trichloroethylene degradation by persulfate in water, where the increase in ferrous iron concentration resulted both in decreased oxidation rate of the contaminant and increased consumption of persulfate. A possible reason for that can be an iron excess that can provide conditions for increased quenching of oxidizing agents (sulfate and hydroxyl radicals, e.g.). Residual dissolved ferrous iron found in the bulk solution after a 24-h persulfate treatment comprised of 0.5-3% of the initial load.

A two-fold increase in ferrous iron dosage (the ratio of H_2O_2/Fe^{2+} changed from 1/0.1 to 1/0.2) with hydrogen peroxide load remained invariable (soil/hydrogen peroxide of 1/0.0012), favored the degradation of DDT with the activated hydrogen peroxide oxidation process (Figure 4). A gradual addition of both, hydrogen peroxide and ferrous iron resulted in some (of 9%) improvement in the DDT degradation level. The treatment with a gradual addition of hydrogen peroxide or ferrous iron only was less effective than that performed with the chemicals added in a single manner or with gradual addition of both indicating excess of either hydrogen peroxide or the activator. It is known (36) that the degradation could be limited by the quenching of $OH^{\bullet}$ with hydrogen peroxide and hydroperoxyl radicals in the presence of hydrogen peroxide excess. Moreover, hydroxyl radical production is also dependent on Fe^{2+}/contaminant ratio that determines the hydroxyl radical/contaminant ratio in an initial rapid degradation phase (14).

While concentration of a residual dissolved ferrous iron measured in the bulk solution after a 24-h treatment with hydrogen peroxide and supplemental ferrous iron comprised of 0.5-5% of the initial load value, a residual hydrogen peroxide was not found. The pH values measured after a 24-h treatment with either hydrogen peroxide or persulfate (Table 2) were somewhat lower in the experiments with the addition of supplementary ferrous iron than that obtained after the treatment with the oxidizing chemical only.

Although Watts and Dilly (28) suggested that ferric iron can be a more effective activator of the hydrogen peroxide oxidation process due to its decreased demand on hydrogen peroxide than the ferrous iron, the addition of supplementary ferric iron did not improve the DDT degradation by either the hydrogen peroxide or persulfate oxidation process (Figs. 3 and 4). The variations in dosages of the chemical (the case of persulfate, Figure 3) or in dosages of ferric iron (the case of hydrogen peroxide, Figure 4) did not affect the degradation of DDT. Nevertheless, complete decomposition of either persulfate or hydrogen peroxide within a 24-h treatment was obtained indicating non-productive consumption of the chemicals. Thus, the application of ferric iron as an activator of the persulfate or the hydrogen peroxide oxidation processes was found to be useless in the present study.

While iron minerals can activate the hydrogen peroxide oxidation of contaminants, they were found (28-31) to be lees reactive than soluble iron. However, it is known (36) that the iron efficiency as the activator is also diminished with the decreasing of the pH due to the reduction of iron solubility. Metal ions chelation is known (14) to promote the chemical oxidation of contaminants at natural soil pH. The primary advantage of the metal ions complexes (44) is the potential for effective generation of hydroxyl radicals at near-neutral pH. Either chelated metal ion complex can be supplementary added or transition metals of soil can be chelated by a complexing agent added. It was hypothesized (37) that chelator-extracted native soil metals can be gradually released and served as the activators for the persulfate oxidation of contaminant. In the study of Wu et al. (45) was also found that EDTA can first chelate and then dissolute metals considerably increasing total organic carbon content in soil bulk solution without a substantial influence on the pH. Dissolution mechanism of iron from iron minerals can be classified according to the solutant type and the reaction that takes place prior to dissolution. Three dissolution mechanisms were distinguished (46): protonation, complexation, and reduction. The potential mechanism of dissolution by complexation was presented (47) on example of iron dissolved from goethite by complex formation with salicylic acid.

The addition of a complexing agent EDTA for the chelation of native transition metals of the soil substantially improved the degradation of total DDT with the hydrogen peroxide oxidation process (Figure 4) and slightly influenced the degradation by persulfate (Figure 3). However, the increase in the ratio of soil/chemical (in case of persulfate, Figure 3) or chemical/EDTA (in case of hydrogen peroxide, Figure 4) did not result in any considerable improvement in the degradation. A lack of natural activator could possible diminish the removal by both the persulfate and hydrogen peroxide oxidation processes.

Complete consumption of persulfate was achieved within 24 h of the treatment with supplementary EDTA addition and the ratio of soil/persulfate = 1/0.0006. This is twice as high as persulfate consumption (52%) obtained within 24 h of the treatment with non-supplemented persulfate at same ratio of soil/ persulfate. Slightly higher persulfate consumption of 83% compared to that of 75% obtained in non-accompanied system was achieved after a 24-h persulfate treatment with supplementary EDTA addition and the ratio of soil/persulfate of 1/0.0024. This increase in persulfate consumption can be explained by an enhanced release of total organic carbon to the bulk solution that also was observed in the study of Wu et al. (45) on the chelating of the soil metal ions by EDTA. Thus, the increased background oxidant demand could probably reduce the oxidation efficiency at higher dosages of chemicals applied. Although Liang et al. (37) have also found that chelated native iron (or other metal ions) was less effective than supplemental chelated iron at enhancing of the persulfate oxidation of contaminant; it can be to some extent useful (48) for practical application.

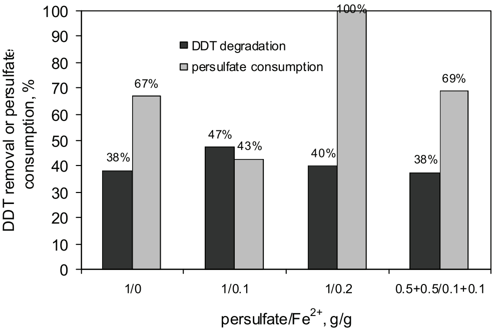

Figure 5. Total DDT removal (% of initial) and persulfate consumption (% of initial) by a 24-h treatment of soil at natural soil pH with persulfate (soil/persulfate of 1/0.0012, g/g) applying supplementary ferrous iron.

While the persulfate oxidation of total DDT activated by supplementary EDTA-chelated ferrous iron was more effective than that by EDTA-native transition metals complex or by supplementary soluble ferrous iron activation aid, the hydrogen peroxide oxidation activated by all the mentioned aids resulted in equal total DDT degradation levels. In addition, the persulfate treatment at a four-fold increase (from 0.0006/1 to 0.0024/1) of persulfate/soil weight ratio and at invariable persulfate/metal ion activator (supplementary unchelated ferrous iron, ferric iron, chelated ferrous iron and chelated native iron or other metal ions) ratio did not result in a higher DDT degradation level (Figure 3).

Thus, possibly due to a lower stability of hydrogen peroxide in the subsurface soluble ferrous iron added gradually can be better utilized in the oxidation system with gradual addition of hydrogen peroxide, while the application of complexed metal activator can promote the oxidation by more stable persulfate.

Complete consumption of persulfate was achieved in the experiments with the application of the chelated ferrous iron. Residual hydrogen peroxide was not found in any of the experiments on metal activation of the hydrogen peroxide oxidation. Opposite to the study of Wu et al. (45) where no any effect of EDTA addition on the pH was observed, the pH increased after the persulfate and hydrogen peroxide treatment in the present study. For example, the application of a 24-h persulfate treatment with the soil/$S_2O_8^{2-}$/EDTA ratios of 1/0.0006/0.000012 and 1/0.0024/0.000048 resulted in the pH values of 6.53 and 6.44, respectively. The pH values of 6.75 and 6.77 were obtained after the hydrogen peroxide treatment with the soil/H_2O_2/EDTA ratios of 1/0.0012/0.000024 and 1/0.0012/0.000048, respectively. These values are higher than the values obtained during the treatment with a single persulfate application and close to that observed after the treatment with a non-accompanied hydrogen peroxide (Table 2).

Alkaline Activation of the Persulfate Oxidation and the Influence of pH on the Hydrogen Peroxide Oxidation

While strong alkaline conditions favored the oxidation with persulfate, acidification to pH of 3.5 enhanced the degradation of total DDT with the hydrogen peroxide oxidation process (Figure 6).

For achieving basic pH needed for the activation of persulfate NaOH, suggested (16) as a better choice than KOH due to the precipitation of formed $K_2S_2O_8$ [49], was added. A possible mechanism for base activation of persulfate was recently proposed by Furman et al. (50). An increase in the pH to a value of 9.0 could slightly (by 4%) improve the degradation of the contaminant. Due to a strong buffering capacity of the soil, the pH decreased during a 24-h treatment from initial 9.0 to 7.6. The adjustment of the pH higher than 11, performed by the addition of NaOH at the weight ratio of soil/NaOH = 1/0.01 (g/g), resulted in a higher total DDT degradation level compared with that achieved by the treatment at natural soil pH (Figure 6). However, the increase in the dosage of persulfate (soil/persulfate weight ratio changed from 1/0.0006 to 1/0.0024) and decrease in the dosage of NaOH (persulfate/NaOH molar ratio changed from 1/80 to 1/20) could diminish the degradation level of the contaminant from 70 to 58%, respectively. Thus, for the effective oxidation of contaminants in soil by base activated persulfate, it is important to optimize not only the ratio of soil/persulfate, but also the ratio of persulfate/NaOH. Thus, elevated dosages of NaOH that take into account the initial soil pH and its buffering capacity should be applied in order to sustain the base activated persulfate oxidation of contaminant. Strong alkaline conditions (pH higher than 10) were also recommended in other studies (16, 34, 38) on the base activated persulfate oxidation. Complete consumption of persulfate was achieved within 24 h of the treatment in alkaline conditions at all the ratios of soil/persulfate applied in the present study.

Slight improvement (from 4% at lower ratio of soil/$S_2O_8^{2-}$ = 1/0.0006 to 8% at higher ratio of soil/$S_2O_8^{2-}$ = 1/0.0024) in the degradation of total DDT was also achieved by the persulfate treatment with a pre-adjustment of the pH to a value of 3.5. It is known (13, 35) that acidic conditions sustain the solubility of natural soil metal mobilized during the strong chemicals oxidation conditions involving them as the activators of the oxidation process. As the system was not buffered, the pH during the treatment somewhat increased (Table 2) with the increasing of the persulfate dosage.

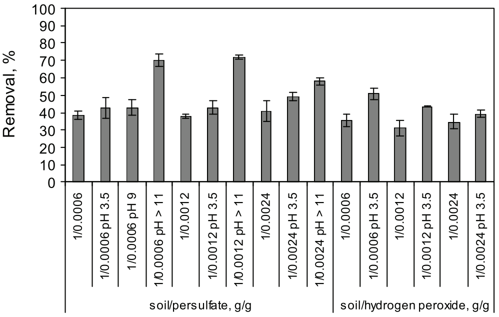

Figure 6. Total DDT removal (% of initial, mean ± standard deviation) by a 24-h treatment of soil with persulfate or hydrogen peroxide at different initial values of pH and weight ratios of soil/chemical.

The influence of the pH on the effectiveness of the hydrogen peroxide oxidation was also investigated. As a rule, acidic pH conditions of 2.0-4.0 favored the oxidation of organic compounds, as it is known that the decomposition rate of hydrogen peroxide reaches the maximum in this pH range (51). This phenomenon is attributed to the progressive hydrolysis of the ferric iron, which provides a relatively large catalytically active surface for contact with H_2O_2 (52). The ferrous iron ion accelerator will yield more hydroxyl radicals in H_2O_2 decomposition. Similar to the treatment with persulfate, the pH during the hydrogen peroxide treatment somewhat increased with the increasing of the hydrogen peroxide dosage (Table 2). This slightly reduced the degradation level of the contaminant (Figure 6), as the productive utilization of hydrogen peroxide may decrease (51) with the increasing of pH.

Complete consumption of either persulfate or hydrogen peroxide was observed after a 24-h treatment at the acidic pH conditions. However, comparing the persulfate and the hydrogen peroxide oxidation systems, a higher removal of total DDT was observed (Figure 6) during the treatment with the application of the base activated persulfate utilizing similar dosages of the chemicals.

Coupling of Biosurfactant with the Persulfate and the Hydrogen Peroxide Oxidation Systems

The addition of biosurfactant, rhamnolipid-alginate complex obtained by biosynthesis of strain *Pseudomonas* sp. PS-17, improved the following degradation of total DDT with both persulfate and hydrogen peroxide (Figure 7). This improvement was probably achieved by the contaminant enhanced desorption to the liquid phase making it available to the oxidizing agents. It was previously found (53) that the applied biosurfactant could stimulate the biodegradation of coal tar waste obtained from former gas work and petroleum residue obtained from atmospheric distillation of light petroleum by increasing the coal tar components bioavailability.

The chemical oxidation of the contaminant was found to be dependent on the biosurfactant dosage (Figure 7). Lower dosage (0.25 g kg^{-1} of soil) of the biosurfactant did not show any improvement in the degradation level of total DDT comparing with that achieved by the treatment with hydrogen peroxide applied alone. The doubling of the biosurfactant dosage from 0.25 to 0.5 g kg^{-1} substantially (by 20%) increased the degradation level. A further increase in the biosurfactant dosage did not influence the efficacy of the hydrogen peroxide oxidation process. The efficacy of the persulfate oxidation was less dependent on the biosurfacatant dosage comparing with that of the hydrogen peroxide process. Although the lowest biosurfactant dosage substantially improved the persulfate oxidation of total DDT, further dosage increase did not show any substantial improvement in the efficacy. Moreover, some reduction in the degradation level was observed at the highest biosurfactant dosage application. Thus, the optimal dosage of biosurfactant differed for the combined treatment utilized hydrogen peroxide and for that utilized persulfate.

While residual hydrogen peroxide was not found in any of the experiments on the hydrogen peroxide treatment, the consumption of persulfate was strongly increased along with dosage of the biosurfactant used. Complete consumption of persulfate was achieved within 24 h of the treatment utilizing the highest (1 g kg^{-1} of soil) dosage of biosurfactant. In this case the chemical could react with biosurfactant increasing the unproductive decomposition of first along with the dosage increase of last. In addition, a wide-range of naturally occurring reactants other than the target contaminant could also be desorbed to bulk solution imposing the increased consumption of the chemical.

Solubility and availability of the transition metals activators could be among the limiting factors in the activation of persulfate and hydrogen peroxide by natural soil metals. There are several studies where biosurfactants in addition to chelating agents were effectively used for enhancing metal removal from soil (54, 55). This gives a presumption for the addition of biosurfactant and chelating agent to soil prior the addition of the chemicals in order to sustain the activation by chelated natural transition metals of soil. As can be seen in Figure 7, the addition of the biosurfactant (0.5 g kg^{-1} of soil), EDTA, and the remedial chemicals could improve the degradation of the contaminant. Thus, the combined application of biosurfactant for increasing of availability and solubility of both contaminant and transition metals of soil, the chelating agent for sustaining metal activity at natural soil pH conditions and the chemicals (persulfate and hydrogen peroxide) for the oxidation of contaminants can be an effective option for contaminated soil remediation.

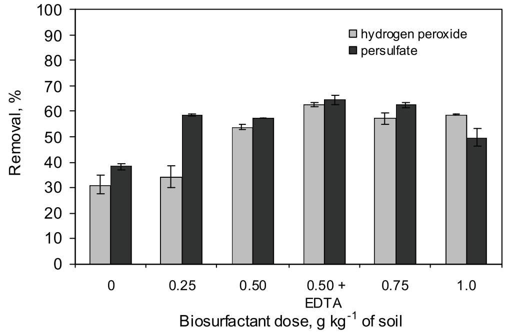

Figure 7. Total DDT removal (% of initial, mean ± standard deviation) by a 24-h treatment of soil at natural soil pH with biosurfactant of different doses and persulfate or hydrogen peroxide at weight ratio of soil/chemical of 1/0.0012. In the experiment with supplementary EDTA the weigh ratio of soil/EDTA of 1/0.000024 was used.

Conclusions

The application of optimized dosages of the chemicals with the properly selected activator aid was found to be important for the effective treatment of contaminated soil with persulfate and hydrogen peroxide.

Total DDT (DDT, DDD, DDE mixture) in soil could degrade with the addition of persulfate or hydrogen peroxide only indicating the potential ability of transition metal ions and minerals of these metals presented in soil to activate the oxidation at natural soil pH (pH of 5.8). However, the degradation of total DDT in soil was uncompleted and independent of the chemicals dosage used.

Higher degradation of total DDT compared to that obtained by persulfate or hydrogen peroxide addition alone was achieved with the addition of supplementary metal activator suggesting a lack of available activator. The use of ferric iron for activation of the persulfate and the hydrogen peroxide oxidation processes did not improve the degradation. While the activation of persulfate by supplementary EDTA-chelated ferrous iron was more effective than by EDTA-native transition metal complex, the treatment efficacy of hydrogen peroxide activated by either of aids was comparable. However, a gradual addition of both hydrogen peroxide and soluble ferrous iron improved the degradation. Thus, added gradually soluble ferrous iron could be effectively utilized in the oxidation system with a gradual addition of hydrogen peroxide, while chelated metal activator promoted the oxidation by more stable persulfate.

The degradation of DDT by a 24-h treatment with persulfate was slightly (by 5%) higher than that with the hydrogen peroxide at similar dosages of the chemicals used. The degradation of DDT with a dual remedial chemical system utilizing both hydrogen peroxide and persulfate was more effective than that with a single chemical application.

The treatment with a solid carrier of hydrogen peroxide, either calcium peroxide or magnesium peroxide, can be an effective alternative to the liquid one resulting in even higher degradation level of the contaminant. A mode of the treatment with the solid carrier of hydrogen peroxide considerably affected the treatment efficacy. A 1-d treatment of soil in slurry with the solid carrier of hydrogen peroxide under a vigorous stirring resulted in a more efficient DDT removal than that in 60%-watered soil.

While acidic pH conditions (pH 3.5) promoted the total DDT degradation with hydrogen peroxide, strong alkaline condition (pH higher than 11) with elevated dosages of NaOH effectively sustained the activated persulfate oxidation of the contaminant.

The addition of biosurfactant, rhamnolipid-alginate complex obtained by biosynthesis of strain *Pseudomonas* sp. PS-17, and EDTA improved the degradation of DDT with both persulfate and hydrogen peroxide at natural soil pH. Thus, the treatment with the combined application of biosurfactant for increasing of availability and solubility of both contaminant and transition metals of soil, the chelating agent for sustaining metal activity at natural soil pH conditions, and the chemicals (persulfate and hydrogen peroxide) for the oxidation of contaminants could be a promising option for the contaminated soil remediation.

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PAPER IV

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Influence of biosurfactant on combined chemical–biological treatment of PCB-contaminated soil

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HIGHLIGHTS

- ▶ EDTA and biosurfactant both improved the removal efficacy of the combined treatment.
- ▶ Biosurfactant addition increased microbial respiration and dehydrogenase activity.
- ▶ Similar removal of PCBs was achieved after a 42-d combined treatment with either H_2O_2 or CaO_2.

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ABSTRACT

The contamination of soil with polychlorinated biphenyl-containing industrial fluids is a worldwide environmental problem due to their high persistence. The present study aimed to elaborate a new strategy of process integration by the joint application of biosurfactant and combined chemical–biological treatment for soil decontamination. The addition of a microbial surfactant from *Pseudomonas* sp. PS-17 to the combined chemical–biological treatment, utilizing liquid hydrogen peroxide or calcium peroxide and a natural consortium of microorganisms-destructors, resulted in process modification that increased the treatment efficacy of soil contaminated with polychlorinated biphenyl-containing electrical insulating oil. A 42-d combined chemical–biological treatment supplemented by biosurfactant addition resulted in an average 47–50% of polychlorinated biphenyls removal – independent of the hydrogen peroxide carrier used. Changes in the soil pH during the combined treatment application with oxidizing chemicals in moderate dosages were unsubstantial. Joint application of the biosurfactant, microorganisms and oxidizing chemicals in moderate dosages increased soil respiration and dehydrogenase activity compared to that obtained by application of the microbial consortium alone, indicating stimulation of microflora by the process integration. The application of the higher calcium peroxide doses (soil/CaO_2 = 1/0.005, g/g) substantially increased the soil pH and diminished soil microbial respiration compared to that for untreated incubated soil. Ethylenediaminetetraacetic acid addition in the experiments with the solid hydrogen peroxide did not affect the treatment efficacy even after the prolongation of the treatment time from 1 to 42 d. Joint addition of both the biosurfactant and the chelating agent to the combined chemical–biological treatment was not effective.

1. Introduction

The contamination of soil by some organic compounds is a great threat to the environment and human health due to disruption of soil structure and inhibition of flora, fauna and microflora. Polychlorinated biphenyls (PCBs) are one of the most dangerous persistent contaminants due to its high bioaccumulation potential [1], high toxicity and carcinogenicity [2] as well as possible endocrine disruptiveness [3]. PCBs were the main component of insulating oil used in electric equipment from the start of their commercial production in 1929 until their banning in many of countries including the USA, the UK and Japan in the 1970s. The widespread use of these compounds led to their substantial release into environments, and effective treatment methods are required.

Various types of remediation procedures including bioremediation [4], chemical oxidation [5], phytoremediation [6] and incineration [7] have been utilized on PCB-contaminated soils with differing degrees of success. There is some evidence that bioremediation can be helpful for decontamination of PCB-contaminated soil. For instance, bioremediation with commercial mixtures of microorganisms [8], separate strains of microorganisms-destructors of hydrocarbons [9] and a lignin-degrading white rot fungus [10] was successfully used to degrade some PCB congeners in soil

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under different aeration conditions. However, low solubility of PCBs and low availability of oxygen in soil result usually in high resistance of PCBs to biodegradation [11].

Some studies of remediation of soil contaminated with PCBs have shown the efficiency of chemical oxidation with ozone [12] and hydrogen peroxide (H_2O_2) [5,13,14]. Recent studies [15,16] have shown that chemical oxidation with calcium peroxide may help overcome problems connected with applying a liquid H_2O_2 carrier, due to controlled prolonged release of H_2O_2 and oxygen. In addition, an optimized application of strong oxidants gives opportunities to utilize the potential of integrated chemical and biological oxidation for contaminated soil remediation. The oxygen release and increase in substrate solubility and nutrient availability to microbial cells during the application of optimized dosages of the chemicals can enhance the aerobic bioremediation of contaminated soil [12,14,16,17]. Complexes of transition metals bound to strong chelating agents such as ethylenediaminetetraacetic acid (EDTA) were found to be effective for the activation of the chemical oxidation promoting the formation of hydroxyl radicals or other oxidants [18,19] and resulting in the improved contaminant degradation in soil [20]. Moreover, it was suggested that the addition of low molecular weight organic acids such as EDTA can disrupt the soil structure through chelation of soil inorganic ions that enhance the bioavailability of organic contaminants to microorganisms [21].

Along with other methods, the application of surfactants has proven effective as a standalone treatment [22] as well as in combination with other methods [23]. Surfactants improve solubilization and desorption behavior of hydrophobic organic compounds and increase their availability (or bioavailability) in contaminated environments [24]. Biosurfactants may substitute their synthetic counterparts in environmental applications due to their biodegradability, low toxicity and high efficiency under various conditions. It was also reported that biosurfactants may enhance biodegradation through enzyme stimulation [25] or promote better permeability of cellular membranes of hydrocarbon-degrading microorganisms [26]. However, this technique has to be integrated in a more complex process to degrade contaminants rather than transferring them to a separate environment. Another promising approach could be the application of microbial surfactants (biosurfactants) to integrated chemical and biological oxidation processes, where they may act as stimulators of oxidation by releasing contaminants adsorbed in soil into the liquid medium and thus increase their availability to oxidizing agents and microorganisms.

Complex approaches involving combined chemical and biological methods and addition of biosurfactants and/or EDTA may be necessary for remediation of heavily contaminated soil. However, the effect of joint application of biosurfactants, and combined chemical–biological treatment remains unknown due to the lack of appropriate studies. In addition, the influence of simultaneous application of biosurfactants and either natural microbial consortia isolated from contaminated media or chemical oxidants on PCBs degradation has not been reported. The rhamnolipid biosurfactants from *Pseudomonas* sp. microorganisms are the most widely studied surface-active products of biological origin, still their influence on chemical oxidation of PCBs in soil was not investigated. In addition, there have been no comparisons of treatment efficacy of PCB-contaminated soil with a solid (calcium peroxide) and a liquid H_2O_2 carrier. The selection of calcium peroxide as an object of the study is conditioned by its relative novelty in the field of chemical oxidation of xenobiotics in the environment and its prolonged effect [15].

Therefore, the present study is devoted to the development of a new strategy of process integration by the joint application of biosurfactant and combined chemical (utilizing H_2O_2) and biological (using a natural consortium of microorganisms-hydrocarbons destructors – MO) treatment for soil decontamination. The effect of addition of EDTA and a microbial surfactant (BS) from *Pseudomonas* sp. PS-17 on the efficacy of treating soil contaminated with PCB-containing oil (Clophen A30), and using a solid carrier (calcium peroxide) or liquid carrier of H_2O_2 was evaluated and compared.

2. Experimental

2.1. Soil sample preparation and characterization

Natural topsoil (0–20 cm) was dried overnight at 30 °C in a circulating air drying-oven before being spiked and sieved through a 2.0-mm sieve using a Retsch (AS 200) digital sieve shaker. The initial pH of soil was 7.3 ± 0.1. Organic carbon and total extractable iron content in the soil were 0.46 ± 0.03 and 12.1 ± 0.9 g kg^{-1}, respectively. Soil pH was determined according to EPA method 9045C [27] and organic carbon by sulfochromic oxidation [28]. Ion-exchangeable Fe(II) fraction and ferrous iron content were 2.0 ± 0.3 mg kg^{-1} and 1.9 ± 0.5 g kg^{-1}, respectively. Ferrous iron and ion-exchangeable Fe(II) fraction were extracted according to Tessier et al. [29]. Total extractable iron in the soil was extracted according to Heron et al. [30]. Iron in the extracts was measured photometrically at 492 nm by phenanthroline method [31]. The texture of the soil was identified as sandy silt (sand content of 45.5%, silt 52% and clay 2.5%), based on the principles established by ISO 14688-1,2 [32,33] using a laser scattering particle size distribution analyzer (LA-950, Horiba). Chloride ion concentration in the initial untreated soil filtrate was 9.0 mg Cl^- kg^{-1} of soil, measured using an ion chromatograph (761 Compact IC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm I.D.) analytical column.

2.2. Soil contaminant

Electrical insulating oil, identified as Clophen A30 – a commercial formulation of PCB congers (19.73% of dichloro-, 48.33% of thrichloro-, 24.55% of tetrachloro-, 6.21% of pentachloro- and 1.18% of hexachlorobiphenyls). PCB congers in the oil were identified using a Shimadzu gas chromatograph mass spectrometer (GC-MS; QP2010 Plus): 1 μL was injected splitless in a Phenomenex capillary (30.0 m × 320 μm I.D. × 0.25 μm film thickness) GC column ZB-5MS. The GC-MS temperature program was as follows: temperature was held at 40 °C for 1 min, then increased at 10 °C min^{-1} up to 120 °C and 4 °C min^{-1} up to 290 °C with a 2-min hold. Injector, interface and ion source temperatures were 250, 260 and 280 °C, respectively. The MS operated in positive chemical ionization mode and scanned between m/z 40 and m/z 340.

Dry soil was artificially spiked with the PCB-containing oil and continuously mixed for 5 h to ensure homogeneous distribution of the contaminant and so better reproducibility in repeated experiments. Then the soil was left for 4 months to aged contamination. The initial concentration of PCB-containing electrical insulating oil, verified by the analysis of eight replicates, was 52 ± 1 g kg^{-1} of dry soil. Oil extraction recovery from the soil was 99 ± 2%.

2.3. Soil treatment

Ten grams of soil were treated without pH pre-adjustment and stirring in a 0.2-L cylindrical glass closed-reactor. All the experiments were carried out in triplicates. Results are presented as mean ± standard deviation.

Calcium peroxide [CaO_2 and $Ca(OH)_2$, powder, 200 mesh (0.075 mm), commercially available product], referred to from here on as CaO_2, purchased from Aldrich, and H_2O_2 (35%), purchased from

Sigma–Aldrich, were the remedial chemicals. The concentration of the active compound, CaO_2, in the technical products determined by the titration of CaO_2 acidic (6% HCl and 14% H_3PO_4) solution by 0.5 N $KMnO_4$ was 76.4 ± 0.1% (with 17.0 ± 0.1% w/w of available oxygen). The concentration of H_2O_2 in stock solution was photometrically verified at 254 nm and calculated using a molar extinction coefficient of 19.6 M^{-1} cm^{-1} [34].

A stock solution of Fe(III)–EDTA with Fe^{3+}/chelate molar ratio of 1/0.6 was prepared by first dissolving of EDTA with the EDTA disodium salt/EDTA tetrasodium salt weight ratio of 2/1 and then of ferric sulfate. The appropriate volume of the stock solution with EDTA concentration of 0.5 g L^{-1} was added to the slurry to achieve the desired dose (0.025 g EDTA kg^{-1} of soil). For the chelating of natural activators present in soil, the EDTA solution utilizing the same dose of EDTA as in the experiments with Fe^{3+}–EDTA complex was added 30 min prior to applying the oxidizing chemicals. The weight ratio of H_2O_2/Fe^{3+} used was 25/1.

The BS was a natural biocomplex of a polysaccharide alginate and of two homologous extracellular glycolipids containing two rhamnose residues and residues of 1-β-hydroxydecanoic acid (Fig. 1) [35]. The BS was produced by biosynthesis of strain *Pseudomonas* sp. PS-17 and then a complex isolation from the culture liquid via acidic precipitation (with 10% HCl at pH 3.0) in the form of 50% concentrate [36]. The BS has a critical micelle concentration (CMC) of 100 mg L^{-1} and surface and interfacial tensions of 29.5 and 0.17 mN m^{-1}, respectively. The CMC was estimated by measuring a surface tension with Du Noüy Ring method using a KRÜSS K6 tensiometer. The interfacial tension was determined in the system water–hexadecane. The BS was added to the samples 24 h prior the application of the chemicals at the dosage of 0.4 g kg^{-1} of soil (i.e. 0.8 g kg^{-1} by weight of the 50% concentrate) to avoid its possible oxidation. The application of the higher dosages of BS (0.8 and 1.6 g kg^{-1}) in the pre-test did not show any influence on PCBs removal efficiency with either H_2O_2 or CaO_2 treatment system.

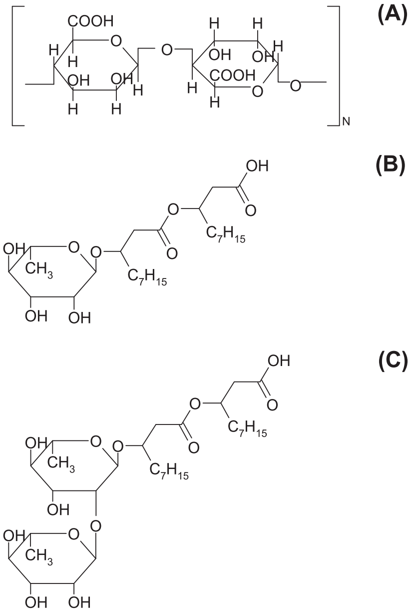

Fig. 1. Structures of the BS components: (A) polysaccharide alginate, (B) monorhamnolipid, and (C) dirhamnolipid.

A natural consortium of microorganisms-destructors of hydrocarbons (MO) was isolated using the method of culture accumulation [37]. The consortium was identified and consisted of two strains: *Rhodococcus* sp. SH-1 and *Arthrobacter* sp. SH-1. The consortium was cultured 1 week before application on the mineral medium with the following composition: 3 g L^{-1} KNO_3, 1 g L^{-1} sodium citrate, 2 g L^{-1} $NaH_2PO_4{\cdot}2H_2O$, 2 g L^{-1} Na_2HPO_4 and 0.5 g L^{-1} $MgSO_4{\cdot}7H_2O$ with PCB-containing oil as a sole carbon source. The consortium cultural liquid was applied to achieve the titer value of approximately 10^7 colony-forming unit (CFU).

The humidity of the soil was kept as 60%. The humidity of 40–70% is considered as optimum for biodegradation process [38]. The soil during the treatment was incubated at 20 °C in the thermostatically controlled cabinet. The volatility of PCBs in soil was not observed during the treatment that can be explained by their low-volatile character according to vapor pressure of $(4–7.7) \times 10^{-5}$ mm Hg at 25 °C [39]. Control was prepared by autoclaving (125 °C for 1 h) the soil twice with a 3-d interval [40]. The control without autoclavation was also used. No any significant effect of indigenous microflora on PCBs removal within 42 d was observed. Soil microbial respiration was measured by oxygen consumption using a Lovibond OxiDirect closed system volumetric respirometer [41]. Dehydrogenase activity (DHA) in soil was measured photometrically at 546 nm by triphenylformazan (TPF) production [42].

2.4. Extraction and determination of electrical insulating oil

After treatment, the solid phase was dried with anhydrous Na_2SO_4 prior to extraction. Dried soil was soaked in 7.5 mL of *n*-hexane and 7.5 mL of acetone (Fischer, analytical grade) and placed for extraction on an orbital shaker (358S, Elpan) overnight. Then a vortex (IKA, Genius3) extraction procedure was used twice (15 mL of hexane each time) for 3 min each. Hexane extract was mixed with internal standard (1/1). The internal standard was 0.6 g L^{-1} nonane in *n*-hexane. A similar PCB-containing oil extraction procedure was carried out for the initial untreated soil.

The concentration of PCB-containing oil in soil was determined using a gas chromatograph (FocusGC, Finnigan, Thermo Electron Corporation) with a flame-ionization detector (FID). Of the extract, 2 μL with the internal standard was injected splitless in a crossbond 100% dimethylpolysiloxane capillary column RTX-1 (30.0 m × 320 μm I.D. × 0.25 μm film thickness). The injector temperature was set to 250 °C. The GC temperature program started at 40 °C, the initial temperature was held for 1 min, then increased by 10 °C min^{-1} to 120 °C, followed by 4 °C min^{-1} to 290 °C and the final temperature was held for 2 min. The detector temperature was 300 °C. The velocity of carrier gas (nitrogen) was 1 mL min^{-1}. The external standard was prepared by dissolving PCB-containing oil in *n*-hexane. Quantification was based on the area count obtained for the merged peaks with the peak start of 11 min and peak end of 50 min. The detection limit of the method was 30 mg oil L^{-1} of hexane that corresponds to 90 mg oil kg^{-1} of dry soil. Oil concentration in the soil was calculated per dry weight. Dry matter in soil samples was determined by oven drying at 105 °C. The GC–FID analyses of un-spiked soil show no indication of contaminants.

3. Results and discussion

3.1. Liquid and solid H_2O_2 carriers for PCB-containing soil treatment

The increase in the dosage of H_2O_2 did not substantially influence the degradation of PCBs within 1 d of the treatment. There was some improvement in PCBs removal (from 17% to 25%) when the weight ratio of soil/H_2O_2 decreased from 1/0.0005 to 1/0.005. The addition of a complexing agent, EDTA, for the chelation of native transition metals in the soil, and of a supplemental Fe^{3+}–EDTA complex, improved (by 7% and 13%, respectively) the degradation of PCBs with a 1-d H_2O_2 treatment – only at the lowest H_2O_2 dosage (soil/H_2O_2 of 1/0.0005, w/w). The addition of EDTA or Fe^{3+}–EDTA complex at the higher H_2O_2 dosages (soil/H_2O_2 of 1/0.005 and of 1/0.025) or by prolonging the treatment time to 42 d did not improve the degradation compared to that of 25% achieved by the 1-d treatment with H_2O_2 addition alone. The potential of naturally occurring soil minerals and transition metals to activate the oxidation by H_2O_2 was previously indicated in several studies [43,44]. Thus, it is important not only to maintain the ratios of H_2O_2 to supplemental activator, but also the ratio of H_2O_2 to soil. The application of moderate H_2O_2 dosages could be recommended in order to avoid its unproductive decomposition. Moreover, optimized application of strong oxidants brings opportunities to utilize the potential of combined chemical and biological oxidation processes for contaminated soil remediation.

Similar to the results of the liquid H_2O_2 treatment there was no reliable effect of increased CaO_2 dosage (weight ratio of soil/CaO_2 decreased from 1/0.0005 to 1/0.025) on contaminant removal. Similar PCBs removal of 13 ± 2% was observed. The addition of the BS (0.4 g kg^{-1}) increased by 4–12% the degradation of PCBs by the CaO_2. The latter could be explained by a possible enhanced desorption of the hydrophobic contaminant to the aqueous phase that increased its availability to oxidizing agents. According to Pacwa-Płocinicza et al. [45] three main mechanisms are involved in the increasing of the availability of organic contaminants in the presence of biosurfactants: (1) facilitated transport of the contaminant from the solid phase, due to lowering of the surface tension of the soil particle and aqueous phase, increase of the contact angle and reduction the capillary force holding contaminant and soil together; (2) dispersion of nonaqueous-phase liquid (NAPL) organics, leading to an increase in contact area caused by a reduction in the interfacial tension between the aqueous phase and the non-aqueous phase; and (3) provision of pseudo-solubility of contaminant, caused by the presence of micelle-bound hydrophobic compound.

The BS addition could also slightly stimulate the oxygen consumption of indigenous microbial populations in soil treated with CaO_2 (Fig. 2). The application of the higher CaO_2 dosage (soil/CaO_2 of 1/0.005, w/w), both alone and with the BS addition, during the treatment of PCB-contaminated soil substantially diminished soil microbial respiration within 28 d of treatment compared to that for untreated incubated soil (Fig. 2). Soil respiration during the treatment at the ratio of soil/CaO_2 of 1/0.0005 was somewhat lower than that in untreated contaminated soil. This also supports the application of moderate dosages of the chemicals for soil decontamination.

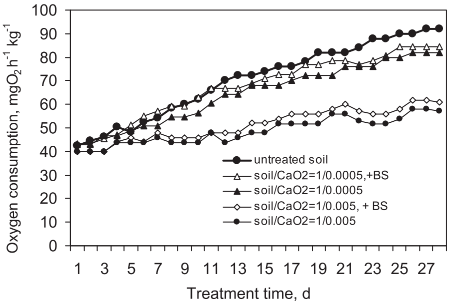

Fig. 2. Oxygen consumption in soil treated with different CaO_2 dosages and the supplementary BS (0.4 g BS kg^{-1} of soil).

Soil buffering capacity was sufficiently strong to keep the soil pH unchanged during application of the lower dosages of CaO_2 (weight ratios of soil/CaO_2 of 1/0.00025 and 1/0.0005). Noticeable pH increase was observed only when the largest CaO_2 dose was added. The application of the higher CaO_2 dose (soil/CaO_2 of 1/0.005, w/w) increased the soil pH from its natural value of 7.3 to 9.6 after a 1-d treatment. This was caused by a higher dosage of $Ca(OH)_2$ added to the soil as a constitute of the CaO_2 powder, as well as, by increased formation of $Ca(OH)_2$ in the reaction of CaO_2 decomposition [16]. However, these changes in the pH did not influence the degradation of PCBs in soil, as similar degradation of PCBs (13 ± 2%) was obtained after 1 d of the treatment applying lower dosages of calcium peroxide. After 21 d of the treatment, the pH of the soil treated with the highest dosage returned to its initial value that confirms the strong buffering capacity of the soil.

The addition of either the BS or EDTA to soil prior to addition of CaO_2 or H_2O_2 may have sustained the activation of the oxidation process by increasing availability and solubility of transition metals present in soil. Moreover, EDTA addition alone was found not only to chelate and mobilize the metals from soil, but also substantially increase the total organic carbon concentration in soil filtrate [46]. This indicates that EDTA, similarly to the BS, may potentially enhance desorption of organic contaminants to the bulk solution, thus improving the following oxidation. While the addition of the BS in the present study could enhance the degradation of the contaminant during a 1-d treatment with either CaO_2 or H_2O_2 (from 15% to 26% and from 17% to 25%, respectively), the addition of EDTA improved the degradation of PCBs by 7% only with liquid H_2O_2. However, CaO_2 is known to release H_2O_2 slowly in the solid phase treatment system with low water content [16] that reduces disproportionation in the H_2O_2 consumption [15], thus a prolonged treatment time should be investigated to evaluate the effect of EDTA addition on the treatment efficacy using the solid carrier of H_2O_2.

3.2. Combined chemical and biological treatment of PCB-contaminated soil

The combined application of chemical and biological treatment for soil decontamination can be more effective than separate application of these approaches [17]. Treatment with H_2O_2 and a natural consortia of microorganisms-destructors isolated from contaminated media was reported to be effective in reducing the concentration of PCBs in soil [13]. However, adding BS to this combined approach can modify the process and increase treatment efficacy of contaminated soil.

The results of the combined application of H_2O_2 or CaO_2 and the hydrocarbon-degrading microbial consortium with and without addition of the BS or EDTA are presented in Fig. 3A and B. Similar to the effect of the BS addition on the chemical treatment the addition of the BS to the biological treatment of soil substantially enhanced the degradation of the contaminants (Fig. 3A and B). In the study of Kang et al. [47] the application of the BS – sophorolipid from *Candida bombicola* was found to stimulate the biodegradation of 2-methylnaphthalene, hexadecane and pristane by increasing their bioavailability in a contaminated model soil.

The combined chemical, utilizing liquid H_2O_2, and biological treatment (MO + H_2O_2) of PCB-contaminated soil was more effective than treatment with microorganisms (MO) only or both MO and the BS (MO + BS) within the 42 d of the treatment period (Fig. 3A). Higher degradation of PCBs was observed after the application of BS and/or EDTA to MO + H_2O_2 system. Despite the degradation of PCBs by the combined chemical–biological treatment with the addition of either EDTA or BS within a prolonged (42 d)

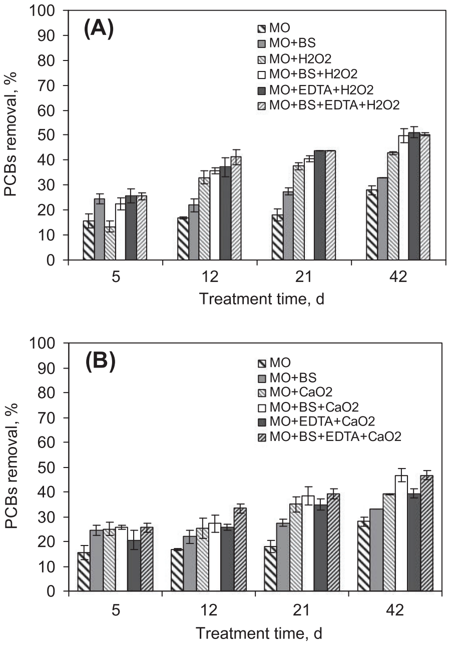

Fig. 3. PCB-containing oil removal by combined chemical–biological treatment system utilizing (A) liquid H_2O_2 and (B) CaO_2 (soil/H_2O_2 of 1/0.0005 w/w, 0.025 g EDTA kg^{-1} of soil and 0.4 g BS kg^{-1} of soil).

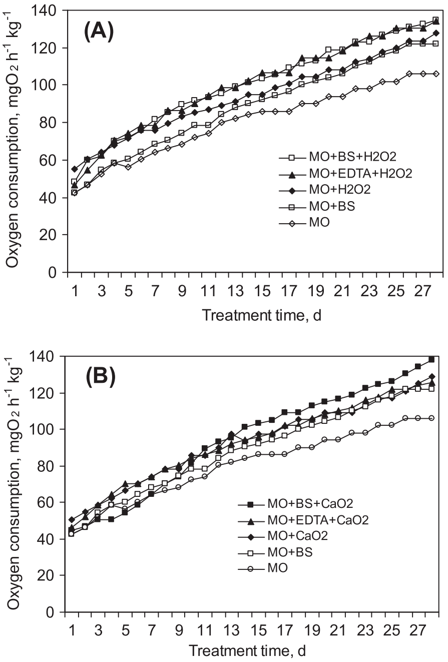

Fig. 4. Oxygen consumption in soil treated with different treatment systems utilizing (A) liquid H_2O_2 and (B) CaO_2 (soil/chemical/EDTA of 1/0.0005/0.000025, w/w/w).

Table 1
DHA in treated soil (soil/chemical of 1/0.0005 w/w, 0.025 g EDTA kg^{-1} of soil and 0.4 g BS kg^{-1} of soil).

Treatment system	DHA (μg TPF h^{-1} g^{-1} of soil) Treatment time (d)		
	12	21	42
MO	17.8 ± 0.9	20.3 ± 0.8	22.9 ± 0.5
MO + BS	19.4 ± 1.1	20.3 ± 0.0	25.1 ± 0.9
MO + H_2O_2	20.6 ± 0.1	23.6 ± 0.1	29.0 ± 0.9
MO + EDTA + H_2O_2	25.8 ± 2.0	26.9 ± 1.1	34.6 ± 1.2
MO + BS + H_2O_2	26.9 ± 0.5	28.2 ± 1.6	34.3 ± 1.3
MO + CaO_2	19.5 ± 1.2	20.3 ± 0.3	24.9 ± 1.0
MO + EDTA + CaO_2	20.3 ± 0.1	22.3 ± 0.6	27.0 ± 0.8
MO + BS + CaO_2	22.0 ± 0.6	26.0 ± 0.4	34.8 ± 0.4

treatment time was close (Fig. 3A), biosurfactants are known to have high biodegradability and biocompatibility [48]. Rhamnolipid that is the main part of the applied BS degrades in soil after 7 d on 92% [49]. EDTA is stable, has low biodegradability and can be substantially absorbed on soil particles [50,51]. These negative side effects of EDTA can potentially make biosurfactants preferable for soil decontamination by combined chemical–biological treatment utilizing H_2O_2. However, similar soil microbial respiration was observed in the experiments with BS and EDTA addition to the combined treatment system with liquid carrier of H_2O_2 (Fig. 4A). The results of treated soil DHA (Table 1) showed that the addition of MO and H_2O_2 with the BS or EDTA stimulated enzymatic activity within 42 d of the treatment, and resulted in a higher DHA than in the systems with microorganisms (MO), microorganisms and the BS (MO + BS) or microorganisms and H_2O_2 (MO + H_2O_2) application only.

The addition of CaO_2 substantially improved the degradation with MO (Fig. 3B). However, the degradation with the combined application of MO and CaO_2 was by 8% lower than that obtained after 42 d of the treatment with MO + BS + CaO_2 and close to that achieved by a 42-d treatment with the combined application of MO, CaO_2 and EDTA (MO + EDTA + CaO_2). While the addition of BS to the MO + CaO_2 system increased the microbial respiration and DHA, no any substantial influence with addition of EDTA was observed (Fig. 4B, Table 1). In general, the addition of microorganisms and CaO_2 has proven less effective at stimulating enzymatic activity than that achieved by joint addition of microorganisms and H_2O_2 (except the case of MO + CaO_2 + BS).

There are several studies showing that the combined application of biosurfactants and chelating agents is effective for enhancing metal immobilization and solubilization [52,53]. The addition of biosurfactants can potentially increase not only the availability of contaminant [54], but also that of soil metals, while the EDTA can provide both the chelation of the metal [52,53] and increase in the soil contaminant availability through the soil structure disruption [26]. The synergistic effect of biosurfactants and EDTA joint addition can potentially result in the increase of contaminant degradation by the combined chemical–biological treatment. However, in the present research the joint application of both the BS and EDTA in the combined chemical–biological treatment did not result in higher degradation of PCBs compared to that of the treatment supplemented by EDTA (except the case MO + EDTA + CaO_2) or the BS addition only (Fig. 3A and B). The slight increase in PCBs removal by MO + EDTA + BS + CaO_2 compared to that by MO + EDTA + CaO_2 was obviously achieved by the BS addition, as similar removal was observed in both systems utilized the BS (MO + EDTA + BS + CaO_2 and MO + BS + CaO_2). Thus, EDTA addition in the experiments with the solid carrier of H_2O_2 did not affect the treatment efficacy even after the prolongation of the treatment time from 1 to 42 d.

Table 2
pH of treated soil (soil/chemical of 1/0.0005 w/w, 0.025 g EDTA kg^{-1} of soil and 0.4 g BS kg^{-1} of soil).

Treatment system	pH ± st. dev. of the mean ($n = 3$) Treatment time (d)			
	5	12	21	42
MO	7.6 ± 0.1	7.3 ± 0.1	7.4 ± 0.1	6.7 ± 0.2
MO + BS	7.7 ± 0.1	7.4 ± 0.1	7.4 ± 0.1	6.9 ± 0.2
MO + H_2O_2	7.1 ± 0.1	7.7 ± 0.1	7.0 ± 0.1	6.8 ± 0.2
MO + BS + H_2O_2	7.0 ± 0.1	7.2 ± 0.1	7.3 ± 0.1	7.4 ± 0.1
MO + EDTA + H_2O_2	7.3 ± 0.1	7.3 ± 0.1	7.8 ± 0.1	7.1 ± 0.1
MO + BS + EDTA + H_2O_2	7.3 ± 0.1	7.3 ± 0.1	7.5 ± 0.1	7.2 ± 0.1
MO + CaO_2	7.8 ± 0.1	7.6 ± 0.1	7.5 ± 0.1	7.2 ± 0.1
MO + BS + CaO_2	7.9 ± 0.1	7.6 ± 0.1	7.6 ± 0.1	6.9 ± 0.1
MO + EDTA + CaO_2	7.1 ± 0.1	7.6 ± 0.1	7.7 ± 0.1	7.1 ± 0.1
MO + BS + EDTA + CaO_2	7.3 ± 0.1	7.5 ± 0.1	7.9 ± 0.1	7.4 ± 0.2

Changes in the soil pH values from the initial value of 7.3 during the combined treatment application were unsubstantial (Table 2). Soil buffering capacity is usually sufficient to resist pH changes during the application of moderate dosages of the chemicals. Moreover, such slight variations in soil pH did not cause stress to microorganisms during the soil treatment (Table 1).

3.3. Effect of biosurfactant addition on the combined chemical and biological treatment

The addition of BS to the combined chemical–biological treatment, utilizing liquid hydrogen peroxide or calcium peroxide and a natural consortium of microorganisms-destructors, resulted in process modification that increased the treatment efficacy of soil contaminated with PCB-containing electrical insulating oil in the present study. In several other studies [54–56] it was shown that BS can improve the bioavailability of non-aqueous and soil-bound phases of PCBs via their desorption and solubilization. It could be assumed that BS can not only increase the bioavailability of PCBs but also their availability to chemical oxidants since both processes are stipulated by similar regularities. The effect of BS addition on the chemical–biological treatment of PCB-contaminated soil is illustrated in Fig. 5. According to the study of Urum et al. [57] the mobilization of the contaminant occurs below the CMC due to the lowering of interfacial tensional between contaminant and water, which further can cause the reduction in capillary force that holds PCBs in soil. Microdroplets of hydrophobic substance as a result of a desorption process (A in Fig. 5) were found [24] in aqueous phase insoluble. Solubilization occurs at a concentration above the CMC, where biosurfactants cluster together, and start forming dynamic aggregates known as micelles [58]. The microdroplets of contaminant (PCB) appear in the core of micelle surrounded by the hydrophobic moieties of the surfactant, while the hydrophilic moieties are directed outside (B in Fig. 5). Biosurfactant can also remove the metals by sorption at the soil interface, followed by desorption of the metal through lowering of soil–water interfacial tension and fluid forces, and following complexation of the metal with the micelles (C in Fig. 5) [51,52]. The increasing availability and solubility of transition metals present in soil may have sustained the activation of the oxidation process. Finally, biosurfactant can stimulate the microbial utilization of contaminant via stimulation of enzymatic activity and increase in permeability of cell membranes (D in Fig. 5).

The process integration achieved by joint application of BS, the oxidizing chemical in moderate dosages and microbial consortium could be a promising option for soil decontamination resulting in improved treatment efficacy. Among the reasons for the increased efficacy of the combined chemical–biological treatment with the BS addition could be desorption and solubilization of the contaminants by the BS, enhancement of the chemical oxidation by increasing availability and solubility of transition metals, the stimulation of microbial activity by both increase in permeability of cell membranes and oxygen released during H_2O_2 decomposition, as well as increased contaminant biodegradability via their partial or complete oxidation by the peroxides.

4. Conclusions

The BS addition enhanced PCBs removal by both chemical and biological treatment of soil; however, the highest removal was achieved by an integrated chemical–biological approach. The joint application of MO, oxidizing chemicals in moderate dosages and the BS resulted in increased soil microbial respiration and DHA, compared to that obtained by the application of the microbial consortium alone – this testifies to the stimulatory effect of the amendments on microflora. The slight variations if any in soil pH support the application of moderate dosages of the chemicals in the combined treatment. The removal of PCBs by a 42-d combined

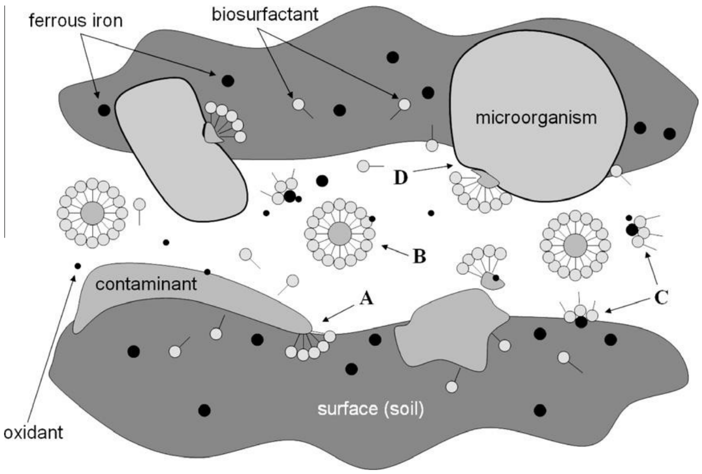

Fig. 5. Effect of BS addition on the chemical–biological treatment of PCB-contaminated soil.

chemical–biological treatment was independent of the carrier of the H_2O_2 when BS was utilized resulting in approx. 47–50% PCBs removal. EDTA addition in the experiments with CaO_2 did not affect the treatment efficacy even after the prolongation of the treatment time from 1 to 42 d. In general, the addition of microorganisms and CaO_2 has proven less effective at stimulating enzymatic activity than that achieved by joint addition of microorganisms and H_2O_2 (except the case of MO + CaO_2 + BS). The joint application of both the BS and EDTA and the combined chemical–biological treatment did not result in higher degradation of PCBs compared to that for the treatment supplemented by EDTA or the BS only.

The present study demonstrated that the joint application of BS, microorganisms and the oxidizing chemicals in moderate dosages resulted in increased PCBs removal compared to that obtained by the single processes applied to this selected test matrix. However, further research on the effect of the BS addition on the removal of various types of organic contaminants by integrated chemical–biological treatment of different types of soil matrices remains to be explored.

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PAPER V

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USE OF HYDROGEN PEROXIDE AND PERCARBONATE TO TREAT CHLORINATED AROMATIC HYDROCARBON-CONTAMINATED SOIL

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Abstract. This study compared treatment methods that utilised a liquid carrier of hydrogen peroxide and a solid carrier, percarbonate, for p-dichlorobenzene, p-chloro-m-cresol and p-chlorothymol degradation in the soil. The targeted chlorinated aromatic contaminants in the soil degraded to a certain level when treated with the liquid hydrogen peroxide, but the removal efficacy was not dependent on the dosage. In contrast, an increase in the percarbonate dosage enhanced the contaminant removal. Supplementary ferrous iron was more effective for the treatment that employed the liquid carrier of hydrogen peroxide than the treatment employing the solid carrier. Although acidic pH conditions (initial pH of 2.5) favoured contaminant degradation using liquid hydrogen peroxide, the treatment involving percarbonate resulted in more effective contaminant removal without any soil pH pre-adjustment. Therefore, the solid carrier of hydrogen peroxide, percarbonate, was concluded to be an effective alternative to the liquid carrier, resulting in greater contaminant removal at natural soil pH values.

Keywords: soil cleaning technologies, chemical oxidation, hydrogen peroxide carrier, activation aid.

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Introduction

Hydrogen peroxide is one of the most popular chemicals used for contaminated soil treatment by chemical oxidation (Watts, Teel 2006). Oxidation with hydrogen peroxide occurs mostly through the generation of free hydroxyl radicals, and the most widespread activator used for the radical pathway is ferrous iron. Hydrogen peroxide activated by ferrous iron is known (Barb *et al.* 1951) as a classical Fenton's reagent, while any deviation from the classical mixture is known as a modified Fenton system. The modified Fenton system has been used to overcome apparent disadvantages in the use of the classical system, including the costly acidic range needed to maintain the radical reactions and the hydroxyl radicals' non-productive consumption, and it is based on the fundamental principles of Fenton chemistry. However, this system may utilise the application of different concentrations of H_2O_2 (2–20%) (Watts *et al.* 1999; Žukauskaitė *et al.* 2012) and carriers of hydrogen peroxide such as CaO_2 (Arienzo 2000; Northup, Cassidy 2008; Goi *et al.* 2011), and it may use chelating agents such as EDTA in addition to transition metals (Sun, Pignatello 1992; Vicente *et al.* 2011). While Fenton's reagent system refers to the iron-mediated hydroxyl radical production from H_2O_2 decomposition, most soil transition metals and ion metals containing minerals (Watts *et al.* 1992) can also activate the hydrogen peroxide oxidation.

The application of sodium percarbonate, $Na_2CO_3 \bullet 1.5H_2O_2$ (hereafter referred to as percarbonate), is another way to modify the Fenton system. Cravotto *et al.* (2007) and Rivas *et al.* (2010) have reported that percarbonate is a solid carrier of hydrogen peroxide with the same features as the liquid carrier, but having safer handling and environmentally friendly procedures. Percarbonate is a crystalline chemical compound that readily dissolves in water, yielding hydrogen peroxide and sodium carbonate (Eq. 1) and creating an alkaline, oxidative environment as a result (McKillop, Sanderson 1995). The actual name of this chemical compound, which reflects the structure of this chemical, is carbonate perhydrate (McKillop, Sanderson 1995).

$$2(Na_2CO_3 \bullet\ 1.5H_2O_2) \rightarrow 2Na_2CO_3+3H_2O_2. \quad (1)$$

It is believed (Rivas *et al.* 2010; McKillop, Sanderson 1995) that the dominant chemistry of the percarbonate oxidation system is that of hydrogen peroxide. Released hydrogen peroxide can oxidise contaminants through the

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formation of hydroxyl radicals or any other oxidative species and is also decomposed to water and oxygen (Eq. 2). Due to the oxygen formation, percarbonate is also used (Vesper *et al.* 1994) to support the aerobic biodegradation of contaminants.

$$2H_2O_2 \rightarrow 2H_2O + O_2. \qquad (2)$$

The sodium carbonate formed in Eq. 1 gives a basic reaction of the carbonate ion hydrolysis in water:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-; \qquad (3)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+. \qquad (4)$$

Rivas *et al.* (2010) have stated that the only potential drawback of $Na_2CO_3 \bullet 1.5H_2O_2$ could be the scavenging of hydroxyl radicals (Eqs 5–7) exerted by the release of (bi)carbonate anions (Eqs 3 and 4). Due to this scavenging, it is believed (Ku *et al.* 1996; Glaze *et al.* 1995) that (bi)carbonate anions have an overall negative impact on the treatment efficacy.

$$HCO_3^- + OH^\bullet \rightarrow HCO_3^\bullet + OH^-; \qquad (5)$$

$$HCO_3^\bullet \leftrightarrow H^+ + CO_3^{-\bullet}; \qquad (6)$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{-\bullet} + OH^-. \qquad (7)$$

However, the carbonate radical anions ($CO_3^{-\bullet}$) generated by reactions 6 and 7 (Umschlag, Hermann 1999) have been reported to yield a reduction potential ($CO_3^{-\bullet}$, H^+/HCO_3^-) of 1.63 V at pH 8.4 (Zuo *et al.* 1999) and have been found (Umschlag, Hermann 1999) to be effective for the degradation of various aromatic compounds, such as benzene, p-xylene, toluene, chlorobenzene, nitrobenzene and benzonitrile. In addition, it has been found (Flangan *et al.* 1986) that bicarbonate anions can also react with hydrogen peroxide to generate peroxymonocarbonate ions (HCO_4^-) (Eq. 8) with an estimated redox potential of 1.8 V (Yao, Richardson 2000) and several other active oxygen species, such as superoxide ions (O_2^-) and singlet oxygen ($^1O_2$).

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O. \qquad (8)$$

A bicarbonate-activated hydrogen peroxide system has been found (Flangan *et al.* 1986; Yao, Richardson 2000; Regino, Richardson 2007) to be capable of oxidising of a variety of organic compounds in the liquid phase. Moreover, the reactivity of HCO_4^- towards organic sulphides has been found (Regino, Richardson 2007) to be higher than that of H_2O_2 by a factor of 100–500 depending on the specific substrates. Thus, the chemistry of the percarbonate oxidation system is more complicated than previously suggested and may allow for the destruction of a wide range of resistant contaminants in soil and water.

There has been only one published study (Cravotto *et al.* 2007) on the application of percarbonate to contaminated soil treatment. This study combined sodium percarbonate and microwaves, resulting in the complete degradation of the aromatic compounds (4-chloronaphtol and 2,4-dichlorophenoxyacetic acid) in the soil. However, unaccompanied applications of microwaves and ultrasound (Duong *et al.* 2010) also had the potential to degrade chlororganic contaminants in soil. As a result, there are no significant studies comparing the efficacy of contaminated soil treatment methods that utilise an unaccompanied solid hydrogen peroxide carrier (percarbonate) and a liquid carrier (hydrogen peroxide).

Chlorobenzenes (CBs) are used in engine-block cleaners, solvents, pesticides, pharmaceutical intermediates and for the synthesis of chlorophenols and disinfectants. Chlorothymols (CTh) are applied as effective fungicide components and chlorocresols (CCr) can be found in metalworking fluids, pharmaceutical products and agricultural pesticides. The extensive use of these compounds has led to their substantial release into the environment (Gomez-Belinchon *et al.* 1991; Jan *et al.* 1994; Kot-Wasik *et al.* 2003; Feidieker *et al.* 1994), necessitating effective treatment methods. The application of liquid hydrogen peroxide has been found (Watts *et al.* 1997, 2008) to be effective for CB-contaminated soil treatment, indicating the need to test the solid hydrogen peroxide carrier, percarbonate, as a potential alternative to the liquid carrier. Although it is known that CBs can degrade in the presence of hydrogen peroxide in soil (Watts *et al.* 2008), the degradation efficacy of CBs, CCr and CTh when utilising hydrogen peroxide in the presence of carbonates/bicarbonates has not been studied.

Therefore, this study performed a comparative assessment of the treatment methods utilising percarbonate and liquid hydrogen peroxide for p-dichlorobenzene (p-DCB), p-chloro-m-cresol (p-C-m-Cr) and p-chlorothymol (p-CTh) removal in soil. The testing of certain activation aids was executed (pH pre-adjustment and supplemental ferrous iron addition) because the activator efficiency depends not only on the target contaminant but also on the remedial chemical used. The influence of chemical dosage on the degradation of selected chlorinated aromatic contaminants was also studied.

1. Methods

1.1. Soil characterisation

Natural topsoil (0–20 cm) was dried overnight at 30 °C in a circulating air drying oven before being spiked and sieved through a 2.0-mm sieve using a Retsch (AS 200) digital sieve shaker. Several characteristics of the soil are presented in Table 1. The soil pH was measured according to EPA method 9045C (1995) using a digital pH meter (CG-840, Schott) equipped with a Mettler Toledo InLaB 412 electrode. The total extractable iron

Table 1. Soil properties

Parameter (unit)	Value (mean ± standard deviation)
pH	5.8
Ferrous iron (g kg^{-1} of soil)	1.9 ± 0.5
Total extractable iron (g kg^{-1} of soil)	12.1 ± 0.9
Ion-exchangeable Fe(II) fraction (mg kg^{-1} of soil)	2.0 ± 0.3
Organic carbon (mg kg^{-1} of soil)	460 ± 30
Sand (%)	45.5
Silt (%)	52
Clay (%)	2.5

in the soil was extracted using the method in Heron *et al.* (1994). Ferrous iron and the ion-exchangeable Fe(II) fraction were extracted according to the procedure presented by Tessier *et al.* (1979) and the iron in the extracts was measured photometrically at 492 nm using the phenanthroline method (Merck 1974). The soil's organic carbon was determined using sulphochromic oxidation (ISO 14235 1998) and the texture of the soil was identified as sandy silt. The soil identification was based on the principles established by ISO 14688-1, 2 (2002, 2004) using a laser scattering particle size distribution analyser (LA-950, Horiba).

The initial concentrations of each individual contaminant in the soil were 0.77 ± 0.03 g p-DCB kg^{-1} of soil, 0.59 ± 0.06 g p-C-m-Cr kg^{-1} of soil and 2.50 ± 0.14 g p-CTh kg^{-1} of soil. Thus, the total concentration of p-DCB, p-C-m-Cr and p-CTh in the untreated soil was 3.86 ± 0.08 g kg^{-1} of soil. The initial concentrations of each target compound were verified by the GC-FID analysis of six replicates.

1.2. Soil treatment

Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$, powder) and hydrogen peroxide (35%) were obtained from Aldrich for this experiment. The comparative assessment of the treatment methods' efficacy when utilising percarbonate and liquid H_2O_2 for the removal of chlorinated hydrocarbons, p-DCB, p-C-m-Cr and p-CTh, was performed by applying similar dosages of H_2O_2. The concentration of H_2O_2 was photometrically verified at 254 nm and the molar extinction coefficient for the hydrogen peroxide at 254 nm taken for the calculation of the H_2O_2 concentration was 19.6 M^{-1} cm^{-1} (Baxendale, Wilson 1957). In the experiments using a supplemental activator addition, $FeSO_4 \cdot 7H_2O$ salt (solution) was used as a ferrous iron source. The ferrous iron concentration in the stock solution was photometrically verified at 492 nm using the complex reaction with 1,10-phenanthrolinium chloride (Merck 1974).

The treatment of p-DCB-, p-C-m-Cr- and p-CTh-contaminated soil with different chemical/contaminant weight (w/w) ratios was carried out in batch mode. The standard procedure entailed a slurry of 10 g soil with 10 mL of liquid (bi-distilled water and remedial chemical solution) being treated in a 0.2-L cylindrical glass reactor using vigorous (300 rpm) magnetic stirring. The treatment time of 24 h was selected to ensure the complete decomposition of hydrogen peroxide. There was no residual hydrogen peroxide after 24 h of treatment. The flasks were sealed with a laboratory film (Parafilm) to reduce volatilisation losses. In the experiments using metal ion-activated hydrogen peroxide oxidation, ferrous iron solution was added and the reaction was initiated by a single addition of the chemical (hydrogen peroxide or percarbonate) solution. The soil was treated without pH pre-adjustment. In the experiments testing the pH effect on the treatment performance, the pH of the soil slurry was pre-adjusted to a value of 2.5 using H_2SO_4.

All of the experiments were carried out at 20 ± 1 °C and in triplicate.

1.3. Extraction and determination of contaminants

The solid and liquid phases were not separated after treatment. Ten mL of hexane were added to the slurry and left overnight on an orbital shaker. Next, a vortex (Genius3, IKA) extraction procedure was employed two times (with 10 mL of n-hexane) for 2 min each. Concentrated hexane extracts were mixed (1/1) with the internal standard, which was $C_{16}H_{34}$ dissolved in n-hexane with a concentration of 0.235 g L^{-1}. The measurement of the contaminant concentration in the extracts was performed using a gas chromatograph (FocusGC, Finnigan, Thermo Electron Corporation) with a flame-ionisation detector (GC-FID). 2 μL of the extract were injected in a crossbond 100% dimethylpolysiloxane capillary column RTX-1 (30.0 m × 320 μm id × 0.25 μm film thickness) at an injector temperature of 260 °C. The GC-FID temperature program included the following steps. The initial temperature was held at 50 °C for 1 min and then increased at a rate of 8 °C min^{-1} to 200 °C with a 3-min hold. The detector temperature was 330 °C and a splitless injection mode was used. The velocity of the carrier gas (nitrogen) was 1 mL min^{-1} and the coefficient of variation for the GC-FID method was 1.5%. The external standard was prepared by dissolving p-DCB, p-C-m-Cr and p-CTh in n-hexane, and the method's detection limit was 11.3 mg p-DCB, 9.0 mg p-C-m-Cr and 7.8 mg p-CTh per L of solvent, which corresponded to 34 mg p-DCB, 27 mg p-C-m-Cr and 26 mg p-CTh per kg of soil. The GC-FID analyses of the un-spiked soil showed no indication of contaminants.

1.4. Soil filtrate analyses

The residual hydrogen peroxide in the soil filtrate treated by titanium sulphate with pertitanic acid formation was determined photometrically at 410 nm (Eisenberg 1943). The pH after the treatment was measured according to EPA method 9045C (1995). The ion content in the soil filtrate was measured using an ion chromatograph (761 Compact IC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm id) analytical column.

2. Results and discussion

2.1. Removal of contaminants with the non-supplemented hydrogen peroxide treatment

p-DCB, p-C-m-Cr and p-CTh in soil degraded with the addition of hydrogen peroxide only (Fig. 1), indicating the ability of the natural activators present in soil to activate the oxidation. The potential for naturally occurring minerals in the soil and some transition metals to activate the hydrogen peroxide oxidation process has been indicated in several previous studies (Matta *et al.* 2008; Watts *et al.* 1997; Kong *et al.* 1998; Teel *et al.* 2001). Nevertheless, the degradation of the contaminants in the soil with liquid hydrogen peroxide was uncompleted, resulting in the same level of contaminant removal regardless of the chemical dosage used (Fig. 1). The removal of p-DCB, p-C-m-Cr and p-CTh with the liquid carrier averaged 10.1 ± 0.7% of the 0.77 ± 0.03 g of p-DCB, 5.9 ± 0.9% of the 0.59 ± 0.06 g of p-C-m-Cr and 22.7 ± 0.8% of the 2.50 ± 0.14 g of p-CTh targeted in each kg of soil.

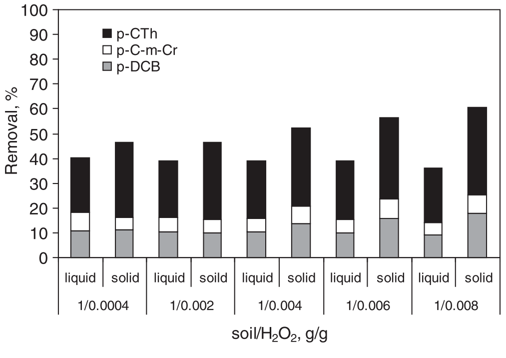


Fig. 1. p-DCB, p-C-m-Cr, and p-CTh removal (% of initial content) in the soil after a 24-h treatment with liquid hydrogen peroxide and percarbonate, without the addition of supplemental ferrous iron and utilising different weight ratios of soil to H_2O_2

A lack of available activators in soil may limit the effective production of hydroxyl radicals and could be a reason for the oxidation reaction termination. The loss of the hydrogen peroxide without the degradation of the contaminants could be explained by competing reactions, such as non-productive chemical decomposition without the generation of oxidants, reaction with the soil's organic matter, etc. (Watts, Teel 2006).

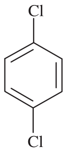
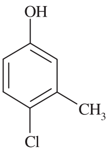
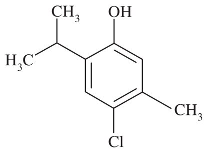
Although the treatment with percarbonate in a study by Rivas *et al.* (2010) has indicated that metoprolol in aqueous solution has the same oxidising power as the liquid hydrogen peroxide, a 24-h soil treatment with percarbonate in the present study led to the improved degradation of p-DCB, p-C-m-Cr and p-CTh compared to that obtained by the treatment with liquid hydrogen peroxide (Fig. 1). The soil treatment with percarbonate at soil/hydrogen peroxide ratios ranging from 1/0.0004 to 1/0.008 allowed for the removal of 10–18% of p-DCB, 5–7% of p-C-m-Cr and 30–36% of p-CTh. Thus, some increase in the removal of each targeted compound was obtained with the application of percarbonate.

The contaminants removal by the percarbonate treatment increased somewhat as the percarbonate dosage increased (Fig. 1). This scenario assumed that several other reactions besides the hydrogen peroxide oxidation were able to proceed. For example, in a study by Regino and Richardson (2007), kinetic and spectroscopic studies of the bicarbonate-catalysed oxidation of organic sulphides have strongly supported the role of peroxymonocarbonate (HCO_4^-) as the oxidant in bicarbonate-activated hydrogen peroxide solution. In a study by Xu *et al.* (2011), bicarbonate anions have also been identified as efficient activators of the hydrogen peroxide oxidation of some organic pollutants, including 4-chlorophenol, providing an efficient transition-metal-free treatment method.

Moreover, certain chemical-physical properties (hydrophobicity, pKa) of the studied compounds, caused primarily by their aromatic nature and functional groups attached to the ring (Table 2), may also have influenced the efficacy. CCr and CTh are weak acids, and their solubility to polar solvents (water) is higher in basic conditions when they are dissociated. The pH increase (Table 3) with the rise in the percarbonate dosage could have resulted in the increased solubility of the target contaminants, which may have influenced the efficacy of the treatment. Increased solubility results in the increased availability of the contaminant to the oxidant, as it is known (Miller, Valentine 1999) that the oxidation reactions proceed mainly in the liquid phase.

The reactivity of the compounds to both applied chemicals followed the order p-C-m-Cr < p-DCB < p-CTh, which could be explained by their chemical structure that influence the rate of oxidizing species attack on the ring, chemical-physical properties of the

Table 2. Chemical-physical properties (molecular weight, water solubility, log K_{ow} and pK_a) of the target compounds

Chemical name and abbreviation	p-dichlorobenzene, 1,4-dichlorobenzene, p-DCB	p-chloro-m-cresol, 4-chloro-3-methylphenol, p-C-m-Cr	p-chlorothymol, 4-chloro-2-isopropyl-5-methylphenol, p-CTh
Structural formula			
Molecular weight (g mol^{-1})	147.0[a]	142.6[a]	184.7[a]
Water solubility at 25 °C (mg L^{-1})	76[a]	3830[a]	89.2[a]
pK_a	–	9.55[a]	9.98[a]
log K_{ow}	3.38[b]	3.10[c]	3.76[d]

[a] Howard *et al.* (1997)
[b] Mackay and Boethling (2000)
[c] Wilfried (2005)
[d] Finizio *et al.* (1997)

contaminants (Table 2) and the difference in the initial concentrations of the target compounds that were also known to have a strong influence on the efficacy of contaminant removal during the Fenton treatment.

2.2. Removal of contaminants with the ferrous iron-supplemented hydrogen peroxide treatment

Higher contaminants degradations, compared to those obtained by unaccompanied liquid hydrogen peroxide, were achieved with the addition of supplemental ferrous iron (Fig. 2a), suggesting a lack of available activators. The increasing Fe^{2+}/H_2O_2 weight ratio, from 0.05/1 to 0.3/1 at lower dosages of liquid hydrogen peroxide (contaminant/$H_2O_2 = 1/0.1$, g/g), did not improve the degradation and even diminished the contaminant removal in the soil (Fig. 2a). This effect was explained by the excessive iron that provided conditions for the increased quenching of oxidising agents (Eq. 9) (Barb *et al.* 1951), reducing the contaminant degradation efficacy as a result.

$$\mathrm{Fe}^{2+} + \mathrm{OH}^{\bullet} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-}. \tag{9}$$

Table 3. pH values of the soil slurry after 24 h of treatment with liquid hydrogen peroxide and percarbonate, with and without a supplemental ferrous iron addition

Contaminant/H_2O_2/Fe^{2+}, w/w/w	pH after 24 h of treatment
Liquid hydrogen peroxide	
1/0.1/0	5.8
1/0.1/0.005	5.7
1/2/0	4.9
1/2/0.1	4.4
Percarbonate	
1/0.1/0	6.2
1/0.1/0.01	5.6
1/1/0	8.5
1/1/0.1	7.8

The increase in the supplemental activator/hydrogen peroxide ratio from 0.05/1 to 0.2/1 at a higher (contaminant/$H_2O_2 = 1/2$, g/g) dosage of hydrogen peroxide improved the degradation of the contaminants from 51.3 ± 3.3 to $73.2 \pm 1.8\%$, respectively. The supplemental ferrous iron addition had a similar effect on the removal of the contaminants during the soil treatment with percarbonate (Fig. 2b). While the increase in the Fe^{2+}/H_2O_2 ratio at a lower ratio of contaminant/$H_2O_2 = 1/0.1$ (w/w) did not improve the degradation, the increase in that ratio at a higher ratio of contaminant/$H_2O_2 = 1/1$ (w/w) considerably increased the removal efficacy. The changes in the contaminant removal efficacy with the addition of the ferrous iron in the percarbonate treatment indicated that the transition metals could also be involved as activators of the oxidation process. The increase in the Fe^{2+}/H_2O_2 weight ratio, from 0.1/1 to 0.3/1, increased the removal of the contaminants from 58.0 ± 0.03 to $80.8 \pm 4.3\%$, respectively. Thus, it was important to optimise not only the hydrogen peroxide/contaminant ratio but also the hydrogen peroxide/transition metal activator ratio for effective contaminant degradation with either carrier of hydrogen peroxide.

In spite of the fact that a supplemental ferrous iron addition could improve the degradation of the contaminants with both carriers of H_2O_2 applying certain ratio of contaminant/H_2O_2/Fe^{2+}, the enhancement of the treatment efficacy was more obvious with the liquid hydrogen peroxide (Figs 2a and 2b). The addition of supplementary ferrous iron to the liquid hydrogen peroxide resulted in a higher removal of all

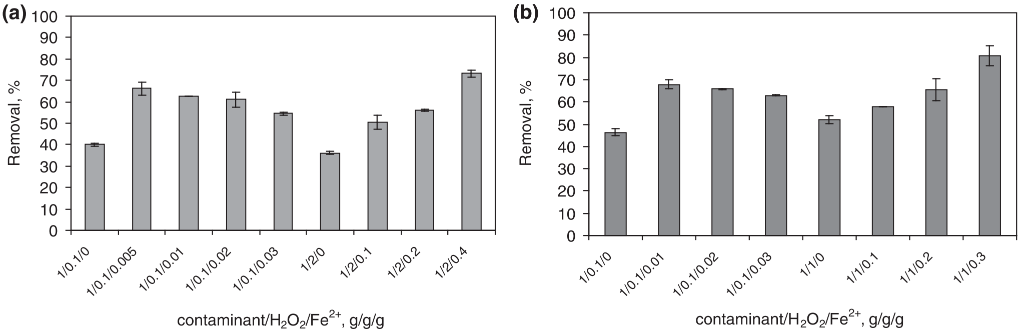


Fig. 2. Total contaminant removal (% of initial content) in the soil after a 24-h treatment with a) hydrogen peroxide and b) percarbonate, with and without the addition of supplemental ferrous iron, at different weight ratios of contaminant-to-H_2O_2. The error bars represent the standard deviation of the replicates (n = 3)

the target compounds compared to that obtained with a single chemical application (Figs 1 and 3). For example, while the removal of p-DCB, p-C-m-Cr and p-CTh with the treatment involving liquid hydrogen peroxide supplemented by a ferrous iron addition was 15–18%, 9–10% and 31–35%, respectively (Fig. 3), the removal of p-DCB, p-C-m-Cr and p-CTh with the treatment involving unaccompanied liquid hydrogen peroxide averaged 10.1 ± 0.7%, 5.9 ± 0.9% and 22.7 ± 0.8%, respectively (Fig. 1).

Increased removal of p-CTh obtained by the treatment with percarbonate supplemented by ferrous iron compared to that achieved by the treatment with a single chemical was noted only. The soil treatment with percarbonate supplemented by ferrous iron allowed for the removal of 47–55% of p-CTh, depending on the chemical dosages used (Fig. 3). The removal of p-CTh with the treatment involving unaccompanied liquid hydrogen peroxide (soil/H_2O_2 = 1/0.0004, g/g) averaged 30% (Fig. 1). On the other hand, the percarbonate application supplemented by ferrous iron showed decreased removal of p-DCB and no influence on the p-C-m-Cr removal (the removal was 4–5% in both cases). While the removal of p-DCB with a single percarbonate treatment was 11% (Fig. 1), the treatment involving the percarbonate-supplementary ferrous iron system removed only 2–4% (Fig. 3). The rates of hydroxyl radical attack on the ring of target compound might be very different depending on the type and degree of substitution. Carbonates may also act as scavengers of the hydroxyl radicals formed in excess during the rapid decomposition of hydrogen peroxide achieved by the addition of a supplementary activator. Thus, unproductive consumption of hydroxyl radicals in side reactions (Watts, Teel 2006) could occur in place of their reaction with the specific target contaminant during the treatment of soil with percarbonate supplemented by ferrous iron. This can result in p-DCB degradation decrease with the addition of supplementary ferrous iron system. Ferrous iron also has had no activation effects in a past study by Cravotto *et al.* (2007) during the percarbonate treatment of 4-chloronaphthol, 2,4-dibromophenol, 2,4-dichlorophenoxyacetic acid and p-nonylphenol contaminated soil.

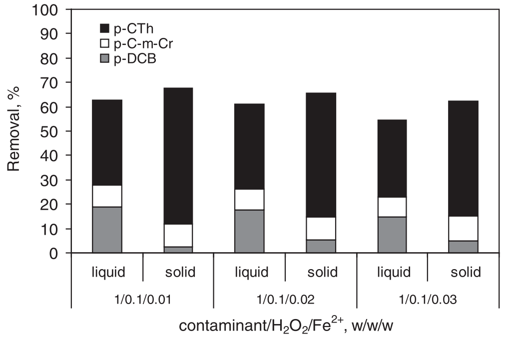


Fig. 3. p-DCB, p-C-m-Cr, p-CTh removal (% of initial content) in the soil after 24 h of treatment with liquid hydrogen peroxide and percarbonate with the addition of supplemental ferrous iron

Thus, the improvement in contaminants total degradation with supplemental ferrous iron addition was more substantial during the treatment with liquid hydrogen peroxide (Figs 2a, b) than with the percarbonate. Lower enhancement in the treatment efficacy with percarbonate could also have occurred because the ferrous iron activation efficacy could be substantially reduced due to the pH increase (Table 3) achieved during the soil treatment with percarbonate. It is known (Sylva 1972) that the Fenton reaction rate tends to decrease as pH increases due to the hydrolysis of iron depending on counter ion, ionic strength, and total iron concentration, culminating in the precipitation of amorphous ferric oxyhydroxides. Thus, the application of a soluble ferrous iron as an activation aid was more effective for the oxidation system utilising liquid hydrogen peroxide.

The results for the soil slurry pH values measured after a 24-h treatment with either liquid hydrogen peroxide or percarbonate are presented in Table 3. The application of a lower dosage of hydrogen peroxide (contaminant/$H_2O_2 = 1/0.1$, g/g) did not influence the soil's pH. The soil's buffering capacity was usually sufficient to offer resistance to pH changes during the decomposition of hydrogen peroxide applied in moderate dosages. However, the treatments with elevated hydrogen peroxide and/or activator dosages have been found capable (Liang *et al.* 2008) of exceeding the buffering capacity of soil. As Table 3 shows, the decrease in soil pH was achieved during the treatment with a twenty-fold increase in the hydrogen peroxide dosage (weight ratio of contaminant/H_2O_2 changed from 1/0.1 to 1/2). A slightly higher decrease in pH, due to the presence of sulphate ions from $FeSO_4$ dissociation, was observed in the experiments involving the addition of a ferrous iron activator. The increased SO_4^{2-} concentration (130–250 mg $SO_4^{2-}L^{-1}$ of the soil filtrate depending on the added ferrous iron sulphate dosage) in comparison with initial value (40 mg $SO_4^{2-}L^{-1}$ of the soil filtrate) was detected in the soil filtrate after the treatment with a supplementary ferrous iron system. On the other hand, the pH of the soil slurry after the treatment with a solid hydrogen peroxide carrier, percarbonate, increased substantially and was greater during the application of higher dosages of percarbonate. A supplementary ferrous iron addition slightly reduced the pH from that achieved by the treatment with a single chemical.

2.3. Influence of soil pH pre-acidification on the removal of contaminants with the hydrogen peroxide treatment

The initial pH of the soil (Table 1) is higher than the optimum pH range of 2–4 identified for the chemical oxidation of chlorinated aromatics using the hydrogen peroxide oxidation process in water (Sedlak, Andren 1991; Ghaly *et al.* 2001). Thus, the treatment of the soil pre-acidified to a pH of 2.5 was tested. Such pre-acidification allowed for the improvement of the contaminant degradation process when using a liquid carrier of hydrogen peroxide (Fig. 4).

The reason for this improvement in contaminant degradation could be that acidic conditions sustain the solubility of natural soil metals mobilised during strong chemical oxidation conditions, involving them as the activators of the oxidation process (Villa *et al.* 2008; Dahnami *et al.* 2006). Moreover, only in acidic conditions the hydroxyl radical is predominant oxidant (Neyens, Baeyens 2003). On the contrary, the percarbonate treatment of the soil at an initial pH of 2.5 resulted in no improvement in the contaminant degradation. Percarbonate dissolves in water and may yield not only hydroxyl radicals but also several other oxidation species (HCO_4^-, $CO_3^{-\cdot}$) that may be more stable at near-neutral pH values (Zuo *et al.* 1999; Yao, Richardson 2000; Regino, Richardson 2007). For example, in a study by Yao and Richardson (2000) on bicarbonate-activated hydrogen peroxide, a maximum catalytic efficacy for the oxidation of organic sulphides was observed at a pH range of 7–9.

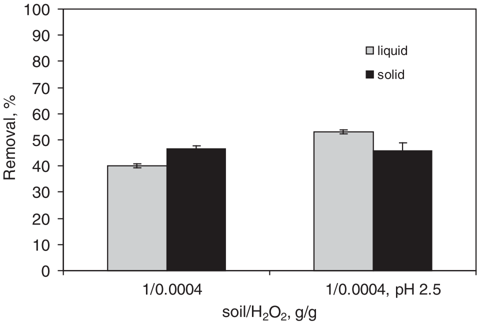


Fig. 4. Total contaminant removal (% of initial content) in soil after 24 h of treatment with liquid hydrogen peroxide and percarbonate at both a natural soil pH and a pH pre-adjusted to 2.5. The error bars represent the standard deviation of the replicates (n = 3)

In summary, the solid carrier of hydrogen peroxide, percarbonate, was employed as an effective alternative to the liquid carrier for the treatment of chlorinated aromatic hydrocarbon-contaminated soil, leading to a higher contaminant degradation level at natural soil pH values. However, further research on the chemistry of the percarbonate process and optimisation of the treatment performance will be required before full-scale treatment of contaminated soil.

Conclusions

This study performed a comparative assessment on the efficacy of using liquid and solid (percarbonate) carries of hydrogen peroxide to treat p-DCB-, CTh- and p-C-m-Cr-contaminated soil. The following conclusions were drawn from the experimental data.

1. The application of liquid hydrogen peroxide to the treatment of chlorinated aromatic hydrocarbon-contaminated soil resulted in $38 \pm 2\%$ total removal of the contaminants, independent of the chemical dosage used. However, increasing the dosage of percarbonate increased the contaminant degradation when allowing several other reactions besides hydrogen peroxide oxidation to proceed.
2. The addition of supplementary ferrous iron increased the contaminant removal efficacy during treatment with both carriers of hydrogen peroxide. However, the improvement in contaminant degradation was more substantial during the treatment with liquid hydrogen peroxide.

3. Pre-acidifying the soil to a pH of 2.5 increased the contaminant degradation during the treatment involving liquid hydrogen peroxide, but did not influence the treatment efficacy of the percarbonate.
4. The results of this study showed that percarbonate could be utilised as an effective alternative to hydrogen peroxide for the treatment of chlorinated aromatic hydrocarbon-contaminated soil at natural soil pH values.

Acknowledgments

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Marika VIISIMAA. Doctoral Student, MSc (chemical and environmental technology, 2010), is the author of 17 scientific publications, 4 of which are ISI Web of Science Publications. Viisimaa underwent research training in the field of soil remediation in Finland and is currently involved in the implementation of several projects on soil remediation and wastewater purification in Estonia. Research interests: chemical treatment of soil, modified Fenton treatment of wastewater.

Anna GOI. Senior Research Scientist, PhD (chemistry and chemical engineering, 2005). Dr Anna Goi is the author of over 70 publications, 21 of which are ISI WEB of Science Publications. Research interests: advanced oxidation processes, combined chemical-biological treatment of soil, wastewater treatment.

APPENDIX B. *CURRICULUM VITAE*

ELULOOKIRJELDUS

1. Isikuandmed

   Ees- ja perekonnanimi: Marika Viisimaa

   Sünniaeg ja -koht: 17. aprill 1986.a., Rapla

   Kodakondsus: eesti

   E-posti aadress: marika.viisimaa@ttu.ee

2. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2010	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2008	Tehnikateaduste bakalaureusekraad
Märjamaa Gümnaasium	2005	Keskharidus

3. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	Emakeel
Inglise keel	Kõrgtase
Vene keel	Algtase
Soome keel	Algtase

4. Täiendusõpe

Õppimise aeg	Täiendusõppe korraldaja nimetus
2012-2013	Tallinna Tehnikaülikool
2010, 2013	Tallinna Keeltekool
2007	VOOG Koolitus ja Konsultatsioon

5. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2012 – k.a.	Tallinna Tehnikaülikool	insener
2009	Tampere Tehnikaülikool	praktikant
2008	Keskkonnaministeerium, Raplamaa Keskkonnateenistus	looduskaitse spetsialist
2007-2008	Keskkonnaministeerium, Raplamaa Keskkonnateenistus	koosseisuväline spetsialist

6. Kaitstud lõputööd

Tehnikateaduste magistrikraad: Polüklooritud bifenüüle sisaldava elektri-isoleerõliga saastatud pinnase taastamine kaltsium- ja magneesium-peroksiididega, Tallinna Tehnikaülikool, 2010. Juhendaja: vanemteadur PhD Anna Goi

7. Teadustöö põhisuunad

1. Bio- ja keskkonnateadused, 1.9. Keskkonnaohtlikke aineid käsitlevad uuringud, T270 Keskkonnatehnoloogia, reostuskontroll (Pinnase taastamine)

8. Teadustegevus

IUT1-7 Keemiatehnikapõhine lähenemisviis prioriteetsete saasteainete ja uute esilekerkivate mikrosaasteainete kõrvaldamisele veest/reoveest ja pinnasest: täiustatud oksüdatsioonitehnoloogiate kasutamine ja optimeerimine (2013 – k.a.)

ETF7812 Klooritud süsivesinikega saastatud pinnase taastamine peroksüdeerimisega (2009 – 2012)

9. Teised uurimisprojektid

AR12017 „Bioloogiliselt raskesti lagunevate ainete kõrvaldamine reoveest füüsikalis-keemiliste ja bioloogiliste meetoditega vesikeskkonna saastekoormuse vähendamiseks” (CHEMBIO) (2013 – k.a.)

Project SF0142719s06 Tehnoloogiliste protsesside intensiivistamine aktuaalsete keskkonnaprobleemide lahendamiseks (2011)

ETF7705 Uus komposiitplastjäätmete taaskasutustehnoloogia (2009)

10. Tunnustused

2014	Tallinna Linnavalitsuse Jaan Poska nimeline stipendium
2013	Parim stendiettekanne FMTDK teaduskonverentsil

11. Juhendatud lõputööd

Jelena Jurjeva, magistrikraad, 2012, (juh) Anna Goi, Marika Viisimaa, Influence of biosurfactant on combined chemical-biological treatment of PCB-contaminated soil (Biopindaktiivsete ainete mõju polüklooritud bifenüülidega saastatud pinnase puhastamisele keemilis-biokeemilise oksüdatsiooniga), Tallinna Tehnikaülikool

Juri Bolobajev, magistrikraad, 2012, (juh) Anna Goi, Marika Viisimaa, Chemical treatment of chlorophene-contaminated soil in columns (Klorofeeniga saastatud pinnase keemiline töötlemine kolonnides), Tallinna Tehnikaülikool

Olga Sõtševskaja, magistrikraad, 2012, (juh) Anna Goi, Marika Viisimaa, Combining of ozone, persulfate and hydrogen peroxide for enhancing of chlorinated hydrocarbons degradation in contaminated soil (Osooni-, persulfaadi- ja vesinikperoksiiditöötluse kombineerimine klooritud süsivesinikke lagundamise intensiivistamiseks saastatud pinnases), Tallinna Tehnikaülikool

CURRICULUM VITAE

1. Personal data

   Name: Marika Viisimaa

   Date and place of birth: 17 April 1986, Rapla

   Citizenship: Estonian

   E-mail address: marika.viisimaa@ttu.ee

2. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2010	Master of Science in Engineering
Tallinn University of Technology	2008	Bachelor of Science in Engineering
Märjamaa Gymnasium	2005	High school education

3. Language competence/skills (fluent, average, basic skills)

Language	Level
Estonian	Fluent
English	Fluent
Russian	Basic skills
Finnish	Basic skills

4. Special courses

Period	Educational or organisation
2012-2013	Tallinn University of Technology
2010, 2013	Tallinna Keeltekool
2007	VOOG Koolitus ja Konsultatsioon

5. Professional employment

Period	Organisation	Position
2012 – to date	Tallinn University of Technology	Engineer
2009	Tampere University of Technology	Trainee
2008	Rapla Environmental Service, Estonia	Environmental Management Specialist
2007-2008	Rapla Environmental Service, Estonia	Specialist

6. Defended theses

MSc thesis: Polychlorinated biphenyls containing electrical insulating oil contaminated soil remediation with calcium and magnesium peroxides, Tallinn University of Technology, 2010. Supervisor: senior researcher PhD Anna Goi

7. Main area of scientific work

1. Biosciences and Environment, 1.9. Research into Substances Hazardous to the Environment, T270 Environmental technology, pollution control (Soil remediation)

8. Scientific work

IUT1-7 Chemical engineering approach to removal of priority pollutants and emerging micropollutants from water/wastewater and soil: implementation and optimization of advanced oxidation technologies (2013 – to date)

ETF7812 Peroxidation for remediation of chlorinated hydrocarbons contaminated soil (2009 – 2012)

9. Other research projects

AR12017 "Degradation of persistent organic pollutants in wastewater with physical-chemical and biological treatment for reduction of pollution load to water bodies" (CHEMBIO) (2013 to date)

SF0142719s06 Intensification of technological processes for the solution of actual environmental problems (2011)

ETF7705 New recycling technology for composite plastic scrap (2009)

10. Awards

2014	Tallinn City Government, Jaan Poska Scholarship
2013	The best poster presentation in FMTDK scientific conference

11. Dissertations supervised

Jelena Jurjeva, Master's Degree, 2012, (sup) Anna Goi, Marika Viisimaa, Influence of biosurfactant on combined chemical-biological treatment of PCB-contaminated soil, Tallinn University of Technology

Juri Bolobajev, Master's Degree, 2012, (sup) Anna Goi, Marika Viisimaa, Chemical treatment of chlorophene-contaminated soil in columns, Tallinn University of Technology

Olga Sõtševskaja, Master's Degree, 2012, (sup) Anna Goi, Marika Viisimaa, Combining of ozone, persulfate and hydrogen peroxide for enhancing of chlorinated hydrocarbons degradation in contaminated soil, Tallinn University of Technology

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and Destruction of Polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase Transformations in Hydrothermal Sintering Processing of Phosphate Rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi Apatites. 1995.

5. **Anu Hamburg**. The Influence of Food Processing and Storage on the N-Nitrosamines Formation and Content in Some Estonian Foodstuffs. 1995.

6. **Ruth Kuldvee**. Computerized Sampling in Ion Chromatography and in Capillary Electrophoresis. 1999.

7. **Külliki Varvas**. Enzymatic Oxidation of Arachidonic Acid in the Coral *Gersemia fruticosa*. 1999.

8. **Marina Kudrjašova**. Application of Factor Analysis to Thermochromatography and Promotion Studies. 2000.

9. **Viia Lepane**. Characterization of Aquatic Humic Substances by Size Exclusion Chromatography and Capillary Electrophoresis. 2001.

10. **Andres Trikkel**. Estonian Calcareous Rocks and Oil Shale Ash as Sorbents for SO_2. 2001.

11. **Marina Kritševskaja**. Photocatalytic Oxidation of Organic Pollutants in Aqueous and Gaseous Phases. 2003.

12. **Inna Kamenev**. Aerobic Bio-Oxidation with Ozonation in Recalcitrant Wastewater Treatment. 2003.

13. **Janek Reinik**. Methods for Purification of Xylidine-Polluted Water. 2003.

14. **Andres Krumme**. Crystallisation Behaviour of High Density Polyethylene Blends with Bimodal Molar Mass Distribution. 2003.

15. **Anna Goi**. Advanced Oxidation Processes for Water Purification and Soil Remediation. 2005.

16. **Pille Meier**. Influence of Aqueous Solutions of Organic Substances on Structure and Properties of Pinewood (*Pinus sylvestris*). 2007.

17. **Kristjan Kruusement**. Water Conversion of Oil Shales and Biomass. 2007.

18. **Niina Kulik**. The Application of Fenton-Based Processes for Wastewater and Soil Treatment. 2008.

19. **Raul Järviste**. The Study of the Changes of Diesel Fuel Properties a its Long Term Storage. 2008.

20. **Mai Uibu**. Abatement of CO_2 Emissions in Estonian Oil Shale-Based Power Production. 2008.

21. **Valeri Gorkunov**. Calcium-Aluminothermal Production of Niobium and Utilization of Wastes. 2008.

22. **Elina Portjanskaja**. Photocatalytic Oxidation of Natural Polymers in Aqueous Solutions. 2009.

23. **Karin Reinhold**. Workplace Assessment: Determination of Hazards Profile using a Flexible Risk Assessment Method. 2009.

24. **Natalja Savest**. Solvent Swelling of Estonian Oil Shales: Low Temperature Thermochemical Conversion Caused Changes in Swelling. 2010.

25. **Triin Märtson**. Methodology and Equipment for Optical Studies of Fast Crystallizing Polymers. 2010.

26. **Deniss Klauson**. Aqueous Photocatalytic Oxidation of Non-Biodegradable Pollutants. 2010.

27. **Oliver Järvik**. Intensification of Activated Sludge Process – the Impact of Ozone and Activated Carbon. 2011.

28. **Triinu Poltimäe**. Thermal Analysis of Crystallization Behaviour of Polyethylene Copolymers and Their Blends. 2011.

29. **Mariliis Sihtmäe**. (Eco)toxicological Information on REACH-Relevant Chemicals: Contribution of Alternative Methods to *in vivo* Approaches. 2011.

30. **Olga Velts**. Oil Shale Ash as a Source of Calcium for Calcium Carbonate: Process Feasibility, Mechanism and Modeling. 2011.

31. **Svetlana Jõks**. Gas-Phase Photocatalytic Oxidation of Organic Air Pollutants. 2012.

32. **Aleksandr Dulov**. Advanced Oxidation Processes for the Treatment of Water and Wastewater Contaminated with Refractory Organic Compounds. 2012.

33. **Aleksei Zaidentsal**. Investigation of Estonian Oil Shale Thermobituminization in Open and Closed System. 2012.

34. **Dmitri Šumigin**. Composites of Low-Density Polyethylene and Poly(Lactic Acid) With Cellulose and Its Derivatives. 2014.