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

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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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 carriers 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 phenanthline 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
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\(_2\)S\(_2\)O\(_8\), 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\(_4\) · 7H\(_2\)O and Fe\(_2\)(SO\(_4\))\(_3\) · 2H\(_2\)O 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\(_2\)SO\(_4\) 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.

### Table 1. Several characteristics of the untreated soil.

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

Values in parentheses denote as total extractable iron (g kg\(^{-1}\) of soil).
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$_2$SO$_4$, 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 (Helios 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 (Helios UV-vis spectrophotometer, Thermo Electron Corporation) at 492 nm by means of 1,10-phenanthroline 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...
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).

\[
S_2O_8^{2-} \rightarrow 2SO_4^{*-} \quad (1)
\]

\[
SO_4^{*-} + H_2O \rightarrow H^+ + SO_4^{2-} + OH^* \quad (2)
\]

\[
OH^* + H_2O_2 \rightarrow H_2O + HO_2^- \quad (3)
\]

\[
HO_2^- + S_2O_8^{2-} \rightarrow O_2 + HSO_4^- + SO_4^{2-} \quad (4)
\]

\[
HO_2^- + H_2O_2 \rightarrow O_2 + H_2O + OH^* \quad (5)
\]

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

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

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

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.
were decomposed within a 24-h treatment at the H$_2$O$_2$/S$_2$O$_5^2$/soil ratios of 0.0012/0.0012/1 and 0.0024/0.0024/1, respectively. Thus, lower ratios of H$_2$O$_2$/S$_2$O$_5^2$/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$_2$O$_2$/S$_2$O$_5^2$ 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$_2$O$_2$ 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).

**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$_2$O$_5^{2-}$/Fe$^{2+}$ of 1/0.0006) was by 11% lower than that obtained by the treatment with the persulfate oxidation activated by supplementary ferrous iron (S$_2$O$_5^{2-}$/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).
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 H₂O₂/Fe²⁺ 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⁻ with hydrogen peroxide and hydroperoxyl radicals in the presence of hydrogen peroxide excess. Moreover, hydroxyl radical production is also dependent on Fe²⁺/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 less 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 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 dissolve 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 possibly 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 the persulfate oxidation of contaminant; it can be to some extent useful (48) for practical application.

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$_2$O$_8^{2-}$/EDTA ratios

![Figure 5](http://example.com/figure5.png)
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/H₂O₂/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 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 K₂S₂O₈ [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/S₂O₈²⁻ = 1/0.0006 to 8% at higher ratio of soil/S₂O₈²⁻ = 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.

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 H₂O₂ (52). The ferrous iron accelerator will yield more hydroxyl radicals in H₂O₂ 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.

**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.
**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 biosurfactant 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.

**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

**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 weight ratio of soil/EDTA of 1/0.00024 was used.

![Figure 7](attachment:image.png)

**Note:** The graph shows the percentage removal of DDT from soil by the biosurfactant at different doses along with persulfate or hydrogen peroxide. The data is presented as mean ± standard deviation.
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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**References**


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