Dechlorination of DDT, DDD and DDE in soil (slurry) phase using magnesium/palladium system

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Abstract

Mg⁰/Pd⁴⁺ was able to dechlorinate >99% of extractable DDT (initial concentration of 10 mg DDT kg⁻¹ of soil) and >90% of extractable DDT (initial concentration of 50 mg DDT kg⁻¹ of soil) in soil slurry. Mg⁰/Pd⁴⁺ was also found to be effective in dechlorinating of 50 mg kg⁻¹ DDD and DDE, in soil aged for varying time periods. GC-MS analyses revealed the formation of 1,1-diphenylethane as an end product from DDT, DDE and DDD. To the best of our knowledge this is the first report describing the application Mg⁰/Pd⁴⁺ system for remediation of DDT, DDD and DDE contaminated soil. We conclude that reductive dechlorination reaction catalyzed by Mg⁰/Pd⁴⁺ may be a promising system to remediate soil contaminated with DDT and its dechlorinated products such as DDD and DDE.

Keywords: DDT; DDE; DDD; Dechlorination; Diphenylethane; Magnesium; Palladium

1. Introduction

DDT (1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), a recalcitrant and toxic pesticide was banned in 1970s for agriculture practices in developed countries. However the pesticide continues to be used in significant quantities in India and other developing countries to control insect borne diseases. DDT and its persistent metabolites (commonly known as DDTr) such as DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane), and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) contaminate soil and create a major environmental problem throughout the world [1]. DDTr reside in soil, bioaccumulate and biomagnify along the food chain and pose risks to ecological components including human beings [2,3].

There are very few studies addressing the degradation of DDTr in soils and most of them are related to photodegradation processes catalyzed by TiO₂. Xie et al. [3] reported that photodegradation of p,p' -DDT by TiO₂ was enhanced by UV light with a reduction in half life from 23.3 to 10.4 h on soil surfaces. The major intermediates identified were p,p'-DDE, p,p'-DDD, and DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethylene). Xu et al. [4] studied the effects of humic substances on photodegradation of DDT in presence of TiO₂ under UV and visible light. Their investigations revealed that in the presence of UV irradiation, humic substances compete with DDT and DDTr and inhibit their mineralization.

Bioremediation is a potential option for the degradation of DDT in soils and slurries. Under anaerobic conditions, DDT is reductively dechlorinated to its major metabolite DDD, which is resistant to further degradation [5]. However, depending upon bioavailability and the presence of efficient biodegrader population, DDD may be further metabolized to DBP (dichlorobenzophenone), which is highly resistant to degradation [5–8]. Under aerobic conditions, DDT is co-metabolically transformed to DDE, a product known to be more persistent than the parent compound [9,10]. Although there are studies showing that numerous soil microbes have the ability to transform DDT in aqueous phase, the pesticide persists in soil due to the non-availability of compound to bacteria. Bioavailability of DDTr is reduced by binding of DDT to soil particles, limited aqueous solubility reducing its diffusion into pore water and lack of appropriate environmental conditions. Weber et al. [11] reported
that three soil properties namely, pH, clay content and total organic matter of soil affect the adsorption of pesticides onto soil. Their studies indicated that in case of nonionizable chlorinated pesticides (like DDT, lindane, diclofenthion, and methoxychlor) only organic matter content determines the extent of pesticides adsorption onto soil. Another significant factor that affects the rate of DDTr mineralization in soil is its ageing i.e. increased contact time between a chemical and soil which allows the compound to bind strongly with soil components (like organic matter, and clay particles) over time. Ageing may also result in the physical entrapment of the compounds in the organic matter or mineral lattice [12,13]. Most studies on DDTr biotransformation have been conducted on freshly added pesticide and are not likely to be reproducible in field conditions where pesticides age for years [10].

An emerging technology that exploits zerovalent metals such as Fe0 or Mg0 for reductive dechlorination of organic halides has drawn the attention of scientific community. There are numerous studies demonstrating successful dechlorination of a wide range of chlorinated compounds like chlorophenols, DDT, PCBs (polychlorinated biphenyls), chlorinated methanes by zero-valent based catalysts [14–19]. The detailed mechanism of this reaction has been proposed by Cheng et al. [15,16]. Dechlorination reaction is typically initiated by ionization of zerovalent metals. In next step, released electrons are captured by protons to generate molecular hydrogen that in turn are dissociatively absorbed onto reducing catalyst (Pd, Ni, Co or Pt) if present, to produce the corresponding metal hydride. The target compounds react rapidly with the metal hydride and are reductively dehalogenated [19]. Major factors that influence the rates and extent of dechlorination by zero-valent metal systems are: (a) ionization potential and  \( E^0 \) of the zero-valent metal, (b) solubility of the metal hydroxide formed following corrosion of metal, (c) presence of oxygen, (d) availability of protons and, (e) solubility of the target compound. Although there are reports on the application of zero-valent metals or bimetallic systems for the dechlorination of chlorinated compounds in aqueous phase, there is scanty information available on the application of above systems for soil phase remediation.

Engelmann et al. [16] and our investigations [20] reveal that Mg0/Pd4+ is able to dechlorinate DDTr all the way to its hydrocarbon product, diphenylethane (DPE) in aqueous phase containing organic solvent or surfactants. However the degradation of DDTr (DDT and its residues) in soil phase presents significant challenges. DDTr is insoluble in aqueous phase, lipophilic in nature and therefore adsorbed onto soil humic substances or enter in micropores of soil particles where they become unavailable for degradation reactions. Non-availability also increases with ageing i.e. increased contact time between soil particles and DDTr which allows the compound to bind strongly with soil components [12]. Hence in the present study, first we studied the extraction efficiency of DDT to ensure the availability of compound for dechlorination reactions, and secondly we evaluated the dechlorination potential of Mg0/Pd4+ bimetallic system in soil slurry. The major objective of the present study was to evaluate the efficiency of Mg0/Pd4+ to dechlorinate DDTr (DDT, DDE and DDD) aged in soil for various time periods.

2. Materials and methods

2.1. Source of chemicals

Magnesium (Mg0) granules (~20 mesh size), K2PdCl6 (hexachloropalladate(IV) dipotassium), DDT (1,1-trichloro-2,2-bis(4-chlorophenyl)ethane, 98.2% pure), DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane, 97.5% pure), and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene, 99.9% pure) were purchased from Sigma-Aldrich Chemical Company. Acetone, glacial acetic acid and cyclohexane were purchased from Merck Ltd. (Mumbai, India). No pretreatment was performed with any chemical and were used as received. JBR biosurfactant was a gift from Jeneil Biosurfactant Ltd, USA. All chemicals were of high purity and analytical grade, unless otherwise specified.

2.2. Collection of soil sample, pretreatment, determination of pH and total organic carbon

Surface soil sample (with no previous history of DDT application) collected from the garden of Centre for Environmental Science and Engineering (CESE), IIT-Bombay, was sieved, dried in oven and autoclaved to inhibit microbial activities. To determine the pH of soil, 1 g of above treated soil was suspended in 10 ml of deionized water, mixed well and allowed to settle. The pH of the supernatant was determined using glass electrode pH meter. Total organic carbon content was calculated by recording the loss of weight of 10 g of autoclaved soil following baking in a muffle furnace at 660 °C for 6 h.

2.3. Ageing of soil amended with DDT, DDD, DDE and treatment with Mg0/Pd4+

To 1 g of autoclaved soil, 10 or 50 µg of DDT or 50 µg of DDD or 50 µg of DDE was added from stock solutions (1000 mg l−1) prepared in acetone. The soil was mixed well for the homogeneous distribution of the target compound following which acetone was allowed to evaporate. These soil samples were allowed to age for varying time periods (01, 10, 20, 30, 60, and 90 days). For dechlorination studies, aged soil samples (1 g) were mixed with solution consisting of 2 ml of acetone and 2 ml of 0.1% biosurfactant following to which Mg0/Pd4+ (10 mg/0.25 mg ml−1) was added. The reaction was initiated by the addition of 416 mM acetic acid and the entire reaction mixture was sealed and incubated for 24 h in a water bath maintained at 130 rpm at 30 °C. In order to account for any other mode of dechlorination in soil, control experiments were conducted under similar conditions as test except that the addition of Mg0/Pd4+ was avoided.
2.4. Extraction of remaining DDT and determination of end product(s) following dechlorination reaction using Mg$^{0}$/Pd$^{4+}$

The entire soil samples were sacrificed following reaction with Mg$^{0}$/Pd$^{4+}$ and extracted using solvent-shake method. As a first step, acetone (4 ml) was added to 4 ml of soil slurry, mixed vigorously and then allowed to settle. The liquid phase was pooled out and collected in pre-cleaned collection glass vial. Second extraction of the soil was done with additional 2 ml of acetone. In second step, the pooled liquid phase (6 ml of acetone + 2 ml of biosurfactant) was then extracted thrice with cyclohexane (8 ml each time, total 24 ml), extracts pooled and analyzed by GC-ECD.

2.5. GC-ECD (gas chromatography–electron capture detection) analyses

Analyses of soil extracts were done using an Agilent model 6890 gas chromatography instrument equipped with Ni$^{63}$ electron capture detector (ECD). The column used was an HP-5 capillary column of 0.32 mm ID, 0.25 µm film thickness and 30 m length. Injection was made in splitless mode using nitrogen as the carrier gas. The following temperature programme was used: the initial oven temperature was 150°C with hold time for 4 min ramped at 6°C min$^{-1}$ up to final temperature of 290°C with hold time for 4 min. The detector temperature was set at 300°C. The residual concentrations of DDT, DDD and DDE were quantified from peak areas obtained through automated integration and also by comparison with known concentrations of standard compounds.

2.6. GC-MS (gas chromatography–mass spectroscopy) analyses

GC-MS analyses were performed using a Perkin Elmer GC-MS (model Clarus 500) instrument interfaced with electron ionization detector. An HP-5 capillary column of 0.32 mm ID, 0.25 µm film thickness and 30 m length was used with helium as the carrier gas. The injection volume was 1 µl. The column temperature was ramped as follows: initial temperature 150°C with hold time for 4 min ramped at 6°C min$^{-1}$ to final temperature of 300°C. The 70 eV electron impact mass spectra were obtained at the maximum of eluted peaks. The mass spectral data coupled to systematic reduction in the retention times of dechlorinated products (due to successive loss of chlorine atoms) allowed identification of the intermediates and end products with reasonable certainty.

3. Results and discussion

Ageing of pesticides in soil often result in the entrapment/occlusion of the compounds in the soil organic matter or mineral lattice. The mechanisms for binding may be formation of covalent bonds, sorption onto soil particles; diffusion into spatially remote areas such as soil macro- and micropores and entrapment within soil organic matter[12,13]. In case of DDT, the most relevant modes of adsorption are expected to be Van der Waals forces and hydrophobic partitioning [21]. Hence as a first step, extraction efficiencies for DDT, DDD and DDE from aged soil were determined. Thereafter reactions were conducted to test the efficacy of Mg$^{0}$/Pd$^{4+}$ for the dechlorination of above listed compounds in soil samples aged for varying time periods.

Extraction efficiencies of DDT from aged soil were found to be ∼53 and ∼70% with 10 and 50 mg kg$^{-1}$ initial concentrations of DDT, respectively, using solvent-shake method. Our results suggest that ageing period (from one to 90 days) does not affect the extraction efficiencies indicating immediate binding of DDT to soil organic matter. Incomplete extraction of DDT may be related to:

(a) Entry of pesticide into micropores of soil particles and its non-availability. The reason for higher extraction efficiency obtained using 50 mg kg$^{-1}$ DDT may be explained on the basis of saturation of micropores with DDT.
Fig. 2. Comparison of GC-ECD profiles of extracts derived from Mg\(^{0}/\text{Pd}^{4+}\) treated (test) soil samples that have been previously spiked with DDT and aged for various time periods. Control represents the profile of extract derived from DDT spiked soil that has been aged for 90 days and not treated with Mg\(^{0}/\text{Pd}^{4+}\). (Conditions: initial concentration of DDT fixed at 50 µg g\(^{-1}\) of soil; soil slurry made in 1:1 acetone:0.1% v/v biosurfactant solution in distilled water; Mg\(^{0}\) = 10 mg ml\(^{-1}\) of soil slurry; K\(_{2}\text{PdCl}_{6}\) = 0.25 mg ml\(^{-1}\) of soil slurry; 416 mM of acetic acid; reaction time = 24 h.)

Table 1

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample Initial DDT concentration (mg l(^{-1}))</th>
<th>Time period of ageing (days)</th>
<th>Concentration of Mg(^{0}/\text{Pd} mg/ mg ml^{-1}) of slurry</th>
<th>Extractable DDT (mg l(^{-1})) from soil</th>
<th>Efficiency of extraction (%) in control samples</th>
<th>Residual DDT (%) (normalized with respect to extraction efficiency following treatment with Mg/Pd)</th>
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\(^{a}\) Controls represent experiments conducted for aged soil spiked with DDT and incubated under same conditions as that of test samples but in the absence of bimetallic system (i.e. no magnesium and palladium was added). Acetic acid (416 mM) was added to all samples.

\(^{b}\) nd: not detected.

\(^{c}\) NA: not applicable.

(b) The organic carbon content of soil was estimated to be 13% and such a high organic content may adsorb huge amount of pesticides irreversibly via diffusion of pesticides into specific sorption sites (holes) within the condensed glass like organic matter as suggested by Xing and Pignatello [22].

(c) During the initial phase of dechlorination reaction, pH of the soil was 3–4. It has been reported that at acidic pH, humic substances make sheet like structures, which trap significant amount of pesticides [23]. This may be a potential reason for incomplete extraction efficiency.

Figs. 1 and 2 compare the GC-ECD profiles of extracts derived from DDT spiked (10 and 50 µg g\(^{-1}\), respectively) soil that has been aged for varying time periods (1–90 days) and subsequently treated with Mg\(^{0}/\text{Pd}^{4+}\) (test). Also the GC-ECD profiles for extracts from control (not treated with Mg\(^{0}/\text{Pd}^{4+}\)) soil samples aged for 30 days and 90 days following spiking with 10 and 50 µg g\(^{-1}\) of DDT, respectively are shown in Figs. 1 and 2. Table 1 presents data related to the extraction efficiencies as well as extent of dechlorination of 10 µg of DDT g\(^{-1}\) of soil and 50 µg of DDT g\(^{-1}\) of soil following aging for various
time periods and subsequent reaction with Mg$^{0}$/Pd$^{4+}$ system. It is evident from the figures and table that Mg$^{0}$/Pd$^{4+}$ is able to dechlorinate $>99\%$ of extractable DDT (if initial concentration of DDT is 10 mg kg$^{-1}$) and $>90\%$ of extractable DDT (if initial concentration of DDT is 50 mg kg$^{-1}$). We were unable to detect any partially dechlorinated intermediates/end product of reaction using GC-ECD.

Fig. 3a (control) shows the GC-MS elution profile for extract derived from DDT spiked (500 µg g$^{-1}$), 5 days aged soil. Fig. 4a (test) shows the GC-MS elution profile for extract derived from DDT spiked (500 µg g$^{-1}$), 5 days aged soil that was treated with Mg$^{0}$/Pd$^{4+}$ for 24 h. Fig. 3a shows the presence of a dominant peak at 19.47 min whose fragmentation pattern matches DDT (Fig. 3b) thereby suggesting the absence of any DDT degradative pathway in soil samples. On the other hand, the...
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1. 30 days aged control (no catalyst)
2. 30 days aged test A (Mg\(^0\) = 10 mg/ml; Pd\(^{4+}\) = 0.25 mg/ml slurry)
3. 30 days aged test B (Mg\(^0\) = 20 mg/ml; Pd\(^{4+}\) = 0.5 mg/ml slurry)

Fig. 6. Comparison of GC-ECD profiles of extracts derived from untreated (control) and Mg\(^0\)/Pd\(^{4+}\) (with two different concentrations) treated soil samples that have been previously spiked with DDD and aged for 30 days. (Conditions: initial concentration of DDD fixed at 50 mg kg\(^{-1}\). Two different concentrations of Mg\(^0\)/Pd\(^{4+}\) used were: (a) Mg\(^0\) = 10 mg ml\(^{-1}\) of soil slurry; K\(_2\)PdCl\(_6\) = 0.25 mg ml\(^{-1}\) of soil slurry, and (b) Mg\(^0\) = 20 mg ml\(^{-1}\) of soil slurry; K\(_2\)PdCl\(_6\) = 0.5 mg ml\(^{-1}\) of soil slurry made in 1:1 acetone:0.1% v/v biosurfactant solution in distilled water containing 416 mM of acetic acid; reaction time = 24 h.)

The above-mentioned peak is absent in Fig. 4a and instead a new peak emerges at 5.46 min. The fragmentation pattern analysis of 5.46 min (Fig. 4b) suggests the presence of the diphenylethane, the hydrocarbon skeleton that is expected to be formed following complete dechlorination of DDT in soil by Mg\(^0\)/Pd\(^{4+}\). The small peak at 8.17 min (Fig. 4a) was identified as 1,1-diphenylethanol based on its fragmentation pattern (Fig. 4c) and this product is expected to be formed via the oxidative route. Dechlorination experiments were also conducted using pellets of Pd\(^0\) (0.05% w/w palladium immobilized on alumina) and we observed only 50% removal of extractable DDT after 24 h of reaction. Due to incomplete degradation of DDT further experiments were not conducted using Pd\(^0\)-alumina pellets.

The extraction efficiencies of DDD and DDE from soil samples were 44 and 74.5% (50 µg of the pesticides g\(^{-1}\) of soil), respectively. The reason for lower extraction efficiency of DDD may be related to its strong interaction with soil components. Fig. 5 compares the GC-ECD profiles for extracts derived from untreated (control) and Mg\(^0\)/Pd\(^{4+}\) treated (test) soil samples that have been previously spiked with DDE and aged for 30 days. Results indicate ~88% dechlorination of DDE by the Mg\(^0\)/Pd\(^{4+}\). Fig. 6 compares the GC-ECD profiles for extracts derived from untreated (control) and Mg\(^0\)/Pd\(^{4+}\) treated (test) soil samples that have been previously spiked with DDD and aged for 30 days. Poor dechlorination (only 44%) of DDD was observed following treatment with lower concentration of Mg\(^0\)/Pd\(^{4+}\) (10 mg/0.25 mg ml\(^{-1}\)). On the other hand, ~95% DDD was degraded following treatment with Mg\(^0\)/Pd\(^{4+}\) (20 mg/0.5 mg ml\(^{-1}\)). Reduced reactivity of DDD may be related to the lower oxidation state of DDD as compared to DDT and DDE.

The dechlorinated products formed in DDE or DDD spiked, 5 days aged soil samples following reaction with Mg\(^0\)/Pd\(^{4+}\) were determined through GC-MS and analyzed according to Weiss and LaPierre [24]. Figs. 7a and 7b depict the GC-MS elution profile of extract derived from control (without treatment with Mg\(^0\)/Pd\(^{4+}\)) soil samples spiked with 500 mg kg\(^{-1}\) DDE and fragmentation pattern of the peak eluting with the retention time of 16.97 min, respectively. The fragmentation pattern of this peak corresponds to DDE thereby suggesting the absence of any DDT degradative pathway in soil samples.

The GC-MS pattern of the extract derived from DDE spiked (500 mg kg\(^{-1}\)) 5 days aged soil following 24 h reaction with Mg\(^0\)/Pd\(^{4+}\) (200 mg/5 mg ml\(^{-1}\)) revealed the presence of a major product peak at 5.46 min and a small peak at 8.17 min (Fig. 8a). Based on the molecular ion fragmentation of the above-mentioned peaks (Figs. 8b and 8c) the end products were identified as 1,1-DPE (diphenylethane), and 1,1-diphenylethanol, respectively.
Fig. 8. (a) GC-MS elution profile of products formed following reaction of DDE spiked (500 mg kg\(^{-1}\)), 5 days aged soil with Mg\(^0\)/Pd\(^{4+}\). (Conditions: Mg\(^0\)/Pd\(^{4+}\) = 200 mg/5 mg ml\(^{-1}\) of soil slurry made in 1:1 acetone:0.1% v/v biosurfactant solution in distilled water in the presence of 416 mM acetic acid, reaction time = 24 h.) (b) GC-MS fragmentation pattern of peak eluting at 5.45 min (see Fig. 8a also). (c) GC-MS fragmentation pattern of peak eluting at 8.17 min (see also Fig. 8a).

Fig. 9a shows the GC-MS elution profile for control (without treatment with Mg\(^0\)/Pd\(^{4+}\)) soil samples spiked with 500 mg kg\(^{-1}\) DDD and aged for 30 days. The peak eluting at 18.40 min was identified as DDD based on its molecular ion fragmentation pattern (Fig. 9b) thereby suggesting the absence of any DDD degradative pathway in soil samples. The GC-MS pattern of extract derived from DDD spiked (500 mg kg\(^{-1}\)) 5 days aged soil sample, following 24 h reaction with Mg\(^0\)/Pd\(^{4+}\) showed the presence of a major product peak eluting at 5.51 min (Fig. 10a). Based on the molecular ion fragmentation of this peak (Fig. 10b) the compound was identified as 1,1-DPE.

Fig. 11 gives a pictorial representation of the mechanism of DDT dechlorination by Mg\(^0\)/Pd\(^{4+}\) in soil slurry phase. First zerovalent magnesium oxidizes to Mg\(^{2+}\) and releases electrons. These electrons are accepted by protons to produce molecular hydrogen which in turn is dissociatively absorbed by the reducing catalyst, palladium (Pd\(^0\)) to generate nascent (atomic) hydrogen. In the next step nascent hydrogen catalyzes reductive dechlorination of DDT all the way to DPE. Presence of acid provides sufficient protons to generate hydrogen and pre-
vents passivation (due to deposition of magnesium hydroxide) of magnesium granules.

Our results support the study by Engelmann et al. [16] who reported the formation 1,1-DPE as end product of Mg/Pd mediated DDT dechlorination in water–acetone phase in acidic environment. We did not observe any ring cleavage products which is in accordance with other reports suggesting that nonchlorinated hydrocarbon skeletons were stable to catalytic dehydrogenation [25,26].

4. Conclusions

Mg\textsuperscript{0}/Pd\textsuperscript{4+} system was able to successfully remediate soil slurry spiked with 10 mg kg\textsuperscript{-1}/50 mg kg\textsuperscript{-1} of DDT or 50 mg kg\textsuperscript{-1} of DDD or DDE and aged for varying time periods (1–90 days). It was observed that the presence of biosurfactant and acetone facilitated optimal rates of DDT, DDD and DDE dechlorination in the slurry phase. In dried soil, reaction rates were extremely slow (data not shown). This is in view of fact that Mg\textsuperscript{0}/Pd\textsuperscript{4+} cannot be homogeneously mixed with dried soil phase. Further the accessibility of Mg\textsuperscript{0}/Pd\textsuperscript{0} surfaces for DDTr dechlorination is very minimal in such a solid phase reaction. The major advantages observed with Mg\textsuperscript{0}/Pd\textsuperscript{4+} system are:

(a) DDT, DDD and DDE spiked in soil can be dechlorinated completely without the accumulation of partially dechlorinated end products.

(b) Reaction rates are significantly faster than the microbiological systems.

(c) No accumulation of partially dechlorinated end products.

(d) No precautions are required to eliminate the presence of oxygen.

Thus reductive dehalogenation (Fig. 11) mediated by Mg/Pd system is a promising method to remediate soil contaminated with DDT, DDE and DDD. However, further studies that aim at biodegradation of the dechlorinated end product, DPE and evaluation of ecotoxicity of Mg\textsuperscript{0}/Pd\textsuperscript{4+} treated soil-slug samples are required prior to field-scale application.

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References