Studies on dechlorination of DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) using magnesium/palladium bimetallic system

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Abstract

The aim of our investigation was to compare the rates of dechlorination of DDT using Mg^0/Pd^{4+} system in two different reaction phases, namely, water–acetone and 0.05% biosurfactant in water. Since palladium is expensive and its toxicity effects are not well known we also examined the reuse efficiency of Pd^0 immobilized on alumina for dechlorinating DDT. Studies on the dechlorination of DDT in water–acetone (1:1, v/v) and 0.05% biosurfactant phases revealed that the reaction followed second order kinetics and rate of reaction is dependent upon both initial concentrations of the target compound and Mg^0/Pd^{4+}. The presence of acid enhanced the rate of reaction by providing protons and preventing passivation of metal that occurs due to deposition of magnesium hydroxide. GC–MS analyses revealed the formation of completely dechlorinated hydrocarbon skeleton of DDT namely, diphenylethane (DPE), as the end product in both reaction phases (water–acetone and 0.05% biosurfactant in water) thereby implying the removal of all five chlorine atoms (three alkyl and two aryl) of DDT. The optimum ratio of water and acetone to facilitate successful dechlorination reaction was found to be 9:1. Results suggested that salt form (K_2PdCl_6) of palladium had higher potential to dechlorinate DDT as compared to pellet (Pd^0–alumina) form (efficiencies of 95 and 36%, respectively, for 100 ppm initial concentration of DDT). We noted that Pd^0–alumina pellets could be reused at least four times for successful dechlorination of DDT provided Mg^0 granules are present in sufficient quantity. Technical grade DDT (50 ppm) containing significant amounts of DDD was dechlorinated almost completely by the Mg^0/Pd^{4+} (10 mg/0.2 mg/ml) within 1 h in water–biosurfactant phase. Our studies reveal that Mg/Pd system is a promising option due to its high reactivity and its ability to achieve complete dechlorination of DDT. This bimetallic system may be useful for designing indigenous permeable barriers or reactors for the treatment of DDT contaminated water.
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1. Introduction

DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) is a potent pesticide used for controlling malaria, typhus, other insect borne diseases and in agriculture. The isomers of this pesticide are released into the environment during manufacture, formulation and usage. "DDT-residues" (DDTr) that collectively represent the different isomers of DDT, DDD, and DDE are now present at numerous sites all around the world [1]. Low solubility, tendency to partition preferentially into lipophilic phase and presence of chlorine atoms make DDTr highly ecotoxic especially to higher organisms [2]. Major mode of toxicity is the attack on central nervous system, interruption with the functions of respiratory system, DNA damage in blood cells and disruption of synthesis and metabolism of endogenous hormones [3–6]. Persistence of DDT residues in the environment, their toxicity to target and non-target organisms, and threat posed to wild life, has led to their classification amongst priority pollutants by various international regulatory agencies.

Over the past two decades there has been intense research around the world to develop methods for remediating DDT. Currently, there is no single method that can satisfactorily address the remediation of DDT under natural environmental conditions. The traditional methods for dechlorination are microbial trans-

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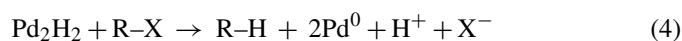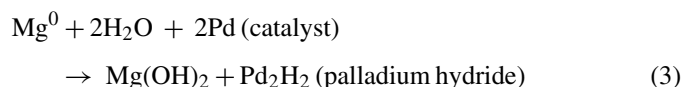[1] Tel.: + 91 22 2576 4854.

formation pathways. However, despite the wide spread use of DDT for more than 50 years, no known microbes have yet evolved to mineralize DDTr completely and use them as sole carbon and energy source. Many studies in literature indicate that various microorganisms isolated from contaminated soil, and waste water exhibit limited ability to transform DDT into partially chlorinated intermediates like DDD, and DDE, which are much more recalcitrant [7–10]. The main contributing factor to the toxicity of DDTr is the presence of chlorine atoms that resist biological degradative reactions [11].

An emerging technology is the use of zero-valent metals and bimetallic systems such as Fe^0, Fe^0/Pd and Mg^0/Pd for dechlorination of pollutants. Number of scientists have reported successful dechlorination of compounds such as polychlorinated biphenyls (PCBs), DDT, chlorinated methanes, chlorinated ethylene and chlorophenols by metal systems. For example Graham and Jovanovic demonstrated dechlorination of p-chlorophenol using Fe^0/Pd in a magnetically stabilized fluidized bed reactor [12]. Engelmann et al. dechlorinated 50 ppm DDT using Mg^0/Pd within 10 min of reaction [13]. In another publication, Engelmann et al. reported simultaneous dechlorination of PCBs and DDT using Fe^0/Pd and Mg^0/Pd sequentially [14]. Initially Fe^0/Pd was employed to partially dechlorinate parent compounds followed by complete dechlorination mediated by Mg^0/Pd. The end products formed were biphenyl and diphenylethane from PCBs and DDT, respectively.

Dechlorination reactions are typically initiated by the ionization of zero-valent metals as shown in reactions (1) and (2):

$$Mg^0 \rightarrow Mg^{2+} + 2e^-, \quad E^0 = -2.2\,V \tag{1}$$

$$Fe^0 \rightarrow Fe^{2+} + 2e^-, \quad E^0 = -0.44\,V \tag{2}$$
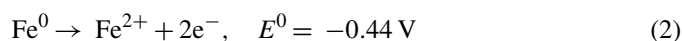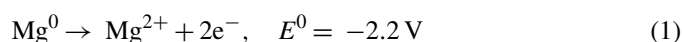
As proposed by Matheson and Tratnyek, in the next step, electrons are captured by protons to generate molecular hydrogen that in turn are presumed to undergo dissociative reaction with catalytic metal (Pd, Ni, Co or Pt) if present, to produce the corresponding metal hydride [15]. The target compounds react rapidly with the metal hydride and are reductively dehalogenated. The above-described reactions are represented below in the following equations:

$$Mg^0 + 2H_2O + 2Pd \,(catalyst)$$
$$\rightarrow Mg(OH)_2 + Pd_2H_2 \,(palladium\ hydride) \tag{3}$$

$$Pd_2H_2 + R–X \rightarrow R–H + 2Pd^0 + H^+ + X^- \tag{4}$$

Thus, the overall reaction in the presence of catalyst (Pd^0) is:

$$M^0 + R–X + H^+ \rightarrow M^{2+} + R–H + X^- \tag{5}$$
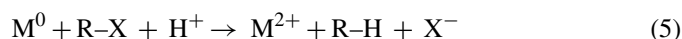
There are four major factors that influence the rates and extent of dechlorination by zero-valent metal systems: (i) ionization potential and E^0 of the zero-valent metal; (ii) solubility of the metal hydroxide formed following corrosion of metal; (iii) presence of oxygen; (iv) availability of protons; (v) solubility of the target compound. With respect to factors (i) and (ii), Mg^0 offers distinct advantages since E^0 for Mg^{+2}/Mg^0 is $-2.2\,V$ (in

comparison to $-0.44\,V$ for Fe^{+2}/Fe^0) and magnesium hydroxide is much more soluble as compared to iron hydroxide. Due to increased solubility, deposition of magnesium hydroxide on magnesium granules and its passivation is relatively slow. With respect to factor (iii), Mg^0 again has distinct advantages since it works in the presence of oxygen (ambient atmosphere) and there is no requirement for creating anoxic or anaerobic conditions. In comparison, anaerobic biological systems and Fe^0 require very low redox potential and may present practical difficulties for on-site remediation. Considering factor (iv), acidic pH is recommended since it ensures availability of adequate protons for generation of H^*. Also acidic pH reduces passivation of metal by enhancing solubility of metal hydroxide. Finally compounds such as DDT require suitable solvent to enhance their solubility, and mass transfer to the hydrogenating catalyst. Solubilizing agents such as acetone or biosurfactant need to be included in the reaction phase.

Engelmann et al. demonstrated dechlorination of DDT by Mg^0/Pd all the way to diphenylethane under acidic conditions using water–acetone as the reaction phase [13]. However, application of this elegant system for remediation of DDTr contaminated water or soil requires further characterization with respect to reaction kinetics and usage of immobilized palladium for recycling since the noble metal is expensive. In addition, the use of organic solvent such as acetone is expensive and also poses health risk. Therefore use of alternate eco-friendly solubilizing agents such as biosurfactants may be a better option. Based on the above considerations we decided to perform further investigations on Mg^0/Pd system. Specific objectives of our investigations were:

- To study the kinetics of dechlorination of DDT using Mg^0/Pd system in water–acetone reaction phase.
- To optimize the water–acetone ratio for DDT dechlorination using Mg^0/Pd^{4+}.
- To study the kinetics of DDT dechlorination using Mg^0/Pd in aqueous reaction phase containing biosurfactant under acidic condition.
- To study the dechlorination of commercial crude (technical grade) DDT mixture using Mg^0/Pd in aqueous reaction phase containing biosurfactant under acidic condition.
- To compare palladium (dipotassium hexachloro palladate(IV) salt) and Pd^0 (immobilized on alumina) for their efficacy to dechlorinate DDT under same conditions.
- To study the reuse efficiency of Pd^0 immobilized on alumina for dechlorinating DDT.

2. Materials and methods

2.1. Source of chemicals

Mg^0 granules (~20 mesh), K_2PdCl_6 (hexachloropalladate(IV) dipotassium), Pd^0–alumina (0.5%, w/w) pellets, DDT (1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene), DDOH (2-bis(p-chlorophenyl)ethanol), DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethy-

lene), and DDA (2,2-bis(*p*-chlorophenyl)acetic acid) were purchased from Sigma–Aldrich Chemical Company and were >98% pure. Acetone, cyclohexane and glacial acetic acid purchased from Merck Ltd. (Mumbai, India) were of analytical grade. No pretreatment was performed with the chemicals and were used as received. JBR biosurfactant was a gift of Jeneil Biosurfactant Ltd., USA. Technical DDT mixture was procured from Hindustan Insecticide Ltd. (HIL), Mumbai, India.

2.2. Dechlorination reaction protocol using Mg^0–Pd^{4+} and analyses

Dechlorination experiments were conducted in 2 ml reaction volume containing desired reaction phases namely, water–acetone (1:1, v/v) or 0.05% JBR biosurfactant in water in the absence and presence of acid, respectively. Appropriate volumes of K_2PdCl_6 stock solution (1 mg ml^{-1}) were diluted into deionized water to attain the required final concentrations (0.05–0.2 mg ml^{-1}). Desired concentrations (30–100 ppm) of DDT were added into reaction tubes from a 1000 ppm stock solution prepared in acetone. Reactions were initiated by the addition of Mg^0 granules (2.5–10 mg ml^{-1}). Instantaneous reduction of Pd^{4+} to Pd^0 was confirmed by the disappearance of reddish color of the salt. All reactions were conducted in triplicate under atmospheric pressure with continuous shaking in a water bath maintained at 30 °C. No precautions were taken to exclude oxygen or reduce redox potential of the reaction phase. Entire reaction mixtures were sacrificed at chosen time points, extracted thrice using cyclohexane (total 6 ml) and 0.2 or 1.0 μl volume of the pooled hexane extracts were injected for GC-ECD analyses to measure the residual concentration of DDT. The identity of dechlorinated end products were confirmed by GC–MS analyses.

2.3. Kinetics of DDT dechlorination using Mg^0–Pd^{4+} system in biosurfactant phase under acidic condition

Kinetic studies were conducted in aqueous phase containing 0.05% of JBR biosurfactant to determine the rates and extent of dechlorination of 84.5, 140.85 and 281.7 μM (30, 50, and 100 ppm, respectively) of DDT at a fixed Mg^0/Pd^{4+} concentration (2.5 mg/0.1 mg ml^{-1}) to establish the order of reaction and compute rate constant (k_{obs}) values. Small volume of acetone that was introduced through addition of DDT from stock solution was evaporated to total dryness. Subsequently the dried DDT was taken up in 0.05% biosurfactant solution in water and reaction conducted as per the protocol described in the previous section. Control experiments were conducted in parallel to determine the extent of DDT degradation, if any, using Pd^{4+} or Mg^0 alone under same conditions as the test samples. Samples were sacrificed at chosen time points, extracted with cyclohexane and analyzed using GC-ECD.

2.4. Kinetics of DDT dechlorination using Mg^0–Pd^{4+} in water–acetone phase (1:1, v/v)

Kinetic studies were conducted in water–acetone (1:1, v/v) phase to determine the rates and extent of dechlorination of

84.5, 140.85 and 281.7 μM of DDT as a function of: (a) varying Mg^0 (2.5, 5.0 and 7.5 mg ml^{-1}) concentrations at a fixed Pd^{4+} concentration (0.05 mg ml^{-1}) and (b) varying Pd^{4+} concentrations (0.05, 0.1 and 0.15 mg ml^{-1}) at a fixed concentration (5 mg ml^{-1}) of Mg^0 to establish the order of reaction and rate constant (k_{obs}) values. The corresponding control experiments were conducted to determine the extent of DDT degradation, if any, using Pd^{4+} or Mg^0 alone under same conditions as the test samples. Samples were sacrificed at chosen time points, extracted thrice in cyclohexane and analyzed for residual DDT, intermediates and end products using GC-ECD.

2.5. Optimization of acetone–water ratio for DDT dechlorination

Optimization of water–acetone ratio was done using reaction system consisting of K_2PdCl_6 (0.1 mg ml^{-1}), Mg^0 (5 mg ml^{-1}), and 50 ppm of DDT. The water–acetone ratios were varied from 1:1 to 19:1 (v/v) and reaction time point of 4 h was chosen to analyze the extent of DDT disappearance in each case.

2.6. Dechlorination of technical DDT mixture in aqueous phase containing 0.01% biosurfactant

Technical grade DDT obtained from Hindustan Insecticide Ltd. (HIL), Mumbai, India was tested for its dechlorination using Mg^0/Pd^{4+} system under acidic condition. The reaction mixture contained DDT (50 ppm), dissolved in 0.01% JBR biosurfactant to which K_2PdCl_6 (0.2 mg ml^{-1}) and acetic acid (333 mM) were added. The reaction was initiated by the addition of Mg^0 (10 mg ml^{-1}). The corresponding control experiments were conducted to determine the extent of DDT degradation, if any, using Pd^{4+} or Mg^0 alone under same conditions as the test samples. The reaction was conducted for 1 h following which samples were extracted with cyclohexane and analyzed for remaining DDT and its dechlorination products by GC-ECD.

2.7. DDT dechlorination efficiency of Pd^0–alumina pellets in comparison to that of K_2PdCl_6 salt

The reaction mixtures (2 ml) consisted of 10 mg Mg^0, 50 or 100 ppm of DDT in 1:1 acetone–water phase, 48 mg of Pd^0–alumina pellet or 0.9 mg K_2PdCl_6 (equivalent elemental weight of Pd in each compound is ~0.24 mg Pd) and 33.3 mM acetic acid. At the end of 30 min of individual reaction, samples were sacrificed, extracted in cyclohexane and analyzed for residual DDT concentration using GC-ECD.

2.8. Reuse efficiency of Pd^0–alumina pellets

The reaction mixture used for first round of reaction consisted of 10 mg Mg^0, 50 ppm DDT in 1:1 acetone–water phase, 48 mg of Pd^0–alumina pellet and acetic acid in 2 ml of 1:1 acetone–water phase. At the end of 2 h of reaction, the entire supernatant was withdrawn, extracted and analyzed for residual DDT concentration by GC-ECD. The Mg^0/Pd^0–alumina pellets were collected, thoroughly rinsed with acetone, dried and

introduced into a fresh reaction mixture consisting of 50 ppm DDT and acetic acid in 2 ml acetone–water (1:1) phase. The above-described metal recycling process, and dechlorination reaction followed by GC-ECD analyses were repeated three more times under identical conditions. The total time period for the first and second round of reaction was 2 h while for the third, fourth and fifth reaction it was 6 h. In total, Mg^0/Pd^0 pellets were cycled through five consecutive reactions, using 2 ml of 50 ppm DDT each time. The strength of acetic acid used was 33.3 mM for the first three reaction cycles and 333 mM for the fourth and fifth cycle.

2.9. Gas chromatography analysis

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

Analyses of extracted samples were done using an Agilent model 6890 gas chromatography instrument equipped with Ni^{63} electron capture detector (ECD). The column used was HP-5 capillary column of 0.32 mm i.d., 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: initial oven temperature of 150 °C with hold time for 4 min, ramped at 6 °C/min 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, partially dechlorinated intermediates and end products were quantified from peak areas obtained through automated integration and also by comparison with known concentrations of pure standard compounds.

2.9.2. GC–MS (gas chromatography–mass spectrometric) analyses

GC–MS analyses were performed using Hewlett Packard model G1800A gas chromatography instrument interfaced with electron ionization detector. HP-1 capillary column was used with helium as the carrier gas. The column temperature was ramped from 150 to 250 °C at 5 °C/min to obtain separation and relative retention time data. Electron impact (70 eV) 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.
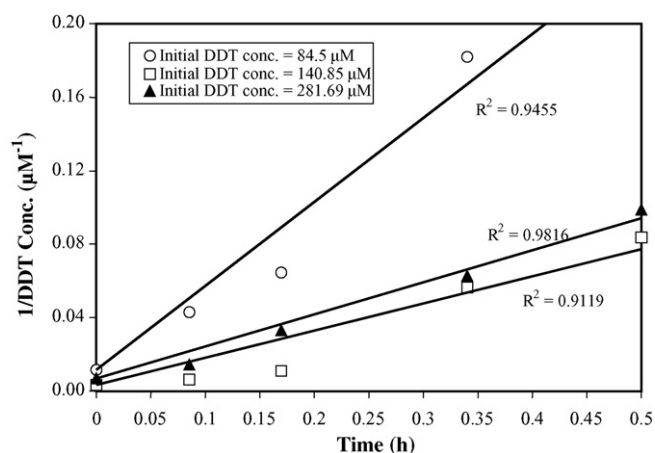

Fig. 1. Kinetic profiles for the dechlorination of DDT (concentrations of DDT as indicated in the figure) using Mg^0–Pd^{4+} (2.5 mg/0.1 mg ml^{-1}) in 0.05% biosurfactant solution in presence of 333 mM acetic acid.

3. Results and discussion

3.1. Kinetics of DDT dechlorination and analysis of endproduct formed using Mg^0–Pd^{4+} system in biosurfactant solution in presence of acid

Preliminary studies conducted with water–biosurfactant solution, indicated that the rates of DDT dechlorination is extremely slow with 40% removal of 50 ppm DDT using Mg^0/Pd^{4+} (10 mg/0.2 mg/ml) in the absence of acid (data not shown). However, addition of acid enhanced the reaction rate significantly presumably by providing adequate concentrations of protons for generation of nascent hydrogen. Therefore, kinetic studies using optimal concentration of Mg^0/Pd^{4+} and different initial concentrations of DDT were conducted in aqueous phase containing 0.05% biosurfactant in the presence of acetic acid. Reactions were extremely fast with >90% removal of 84.5, 140.85 and 281.7 μM of DDT within 30 min. The initial velocity plots as shown in Fig. 1 suggest second order kinetics. The second order rate constants (see last row of Table 1) decreases with increasing initial concentrations of DDT, possibly due to excessive deposition of the target compound on surface of magnesium or magnesium/palladium granules and reduced corrosion of the zero-valent metal. The identity of intermediates and end products formed following reaction of DDT with Mg^0/Pd^{4+} for 1 h

Table 1
Calculated second order rate constants for the removal of DDT using varying concentrations of K_2PdCl_6/Mg^0

| S. no.	[K_2PdCl_6] (mg ml^{-1})	[Mg^0] (mg ml^{-1})	Solvent phase	Second order rate constant (k_{obs}, μM^{-1} h^{-1}) at various initial concentrations of DDT (μM). Initial concentration of DDT (μM)		
				84.5	140.85	281.7
	0.05	2.5	Water–acetone (no acid)	0.02	0.008	0.003
2	0.05	5.0	Water–acetone (no acid)	0.038	0.016	0.0036
3	0.05	7.5	Water–acetone (no acid)	0.038	0.020	0.0082
4	0.1	5.0	Water–acetone (no acid)	0.08	0.0265	0.014
5	0.15	5.0	Water–acetone (no acid)	0.09	0.045	0.012
6	0.1	2.5	Aqueous phase containing 0.05% biosurfactant + 333 mM acetic acid	0.46	0.174	0.15

Rate constants were derived from initial velocity plots.
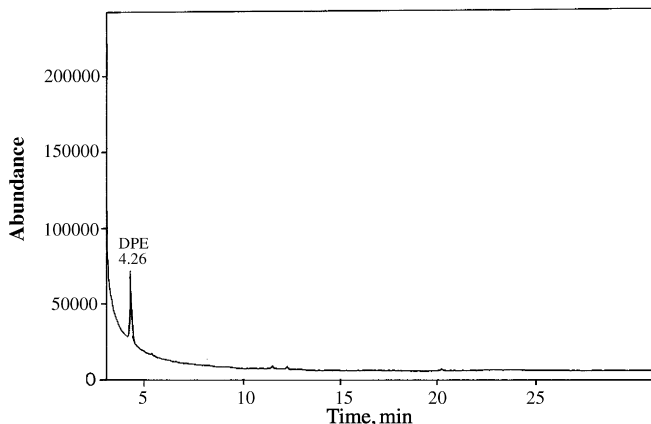
Fig. 2. GC–MS elution profile of product formed following 1 h reaction of 50 ppm DDT with Mg^0–Pd^{4+} (10 mg/0.2 mg ml^{-1}) in 0.01% biosurfactant phase in presence of 333 mM acetic acid.

Fig. 4. Kinetic profiles for DDT dechlorination using varying concentrations (as indicated in the figure) of Mg^0–K_2PdCl_6 in water:acetone (1:1) phase in the absence of acid. Initial concentration of DDT was fixed at 84.5 μM.

were determined through GC–MS (Figs. 2 and 3) and analyzed according to Weiss and Lapierre [16]. Based on the molecular ion fragmentation pattern of the product peak eluting at 4.26 min (Fig. 2) the compound formed after dechlorination of DDT was identified as DPE (diphenyl ethane), characterized by m/z of 182 (Fig. 3). A base peak of m/z 167 is expected to be formed by the elimination of $CH_3^\bullet$ from DPE. The presence of this base peak in Fig. 3 is an evidence for the formation of DPE as the end product of dechlorination reaction. Formation of DPE as the end product suggests removal of three alkyl and two aryl chlorine atoms, which may occur simultaneously or sequentially. If one assumes sequential dechlorination, the time intervals between two successive reductive dechlorination steps appear to be too fast to permit the accumulation and detection of partially dechlorinated intermediates. Dechlorination reaction is presumably mediated via heterogeneous phase catalysis wherein DDT is adsorbed from the liquid phase onto the Md^0/Pd^0 surfaces and dechlorinated to the end product, DPE. The use of biosurfactant offers additional advantages since it is biogenic and expected to biodegrade. Additionally biosurfactant may be less expensive in term of application for treating large quantities of DDT. Sayles et al. calculated first order rate constants for dechlorination of DDT using powdered zero-valent iron (Fe^0) under anaerobic condi-

tions in the absence and presence of surfactant, triton X-114 [17]. Rate constant values observed with and without surfactant were 1.7 and 3.0 d^{-1}, respectively. The research group proposed dechlorination of DDT via direct electron transfer. The lower rate constants observed by Sayles et al. may be attributed to: (a) lower rate of electron transfer and dechlorination by Fe^0 and (b) precipitation of iron hydroxide under alkaline conditions and inhibition (passivation) of Fe^0 corrosion.

3.2. Kinetics of DDT dechlorination and analysis of end product formed using Mg^0–Pd^{4+} system in water–acetone (1:1, v/v) phase in the absence of acid

Figs. 4–6 illustrate the second order kinetic plots (similar to those obtained for DDT dechlorination in biosurfactant phase) for dechlorination of 84.5, 140.85, 281.7 μM DDT with varying concentrations of Mg^0 (at a fixed concentration of K_2PdCl_6) and with varying concentrations of K_2PdCl_6 (at fixed concentrations of Mg^0). The second order rate constant values (k_{obs}) are listed in Table 1 and analysis reveals the following points: (a) reduction in the rate constant values with increasing the concentrations
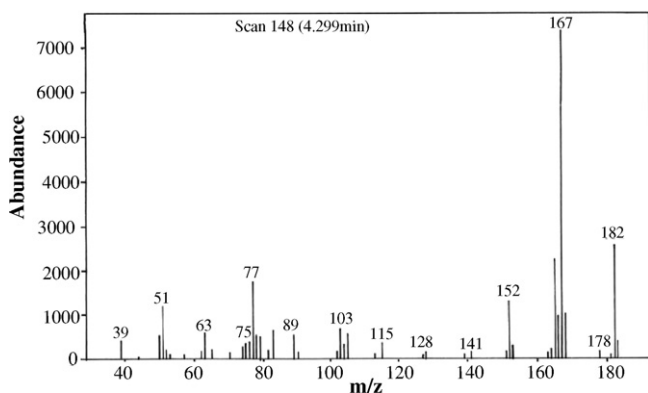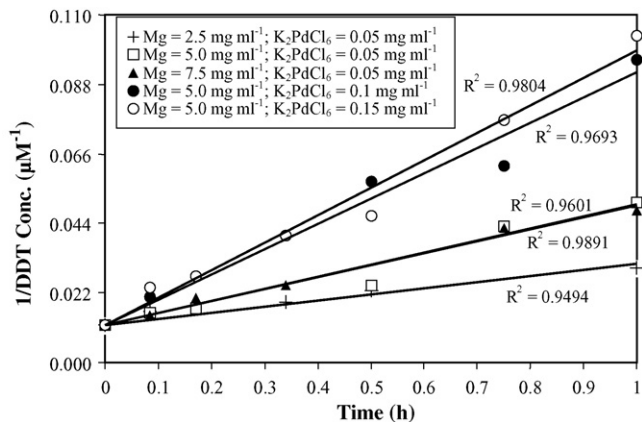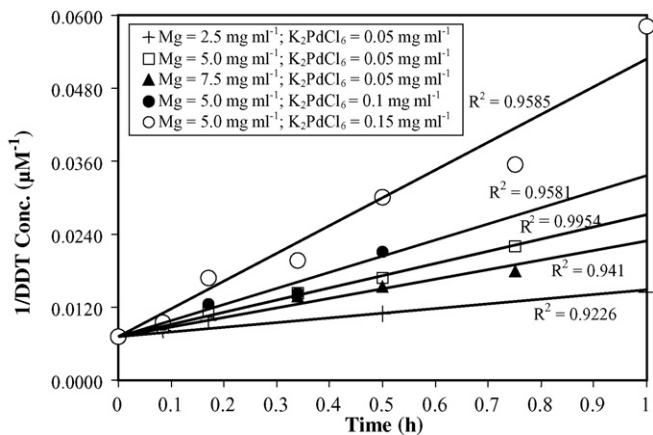

Fig. 3. GC–MS fragmentation pattern for the product peak eluting at 4.26 min (see Fig. 2 also).

Fig. 5. Kinetic profiles for DDT dechlorination using varying concentrations (as indicated in the figure) of Mg^0–K_2PdCl_6 in water:acetone (1:1) phase in the absence of acid. Initial concentration of DDT was fixed at 140.85 μM.
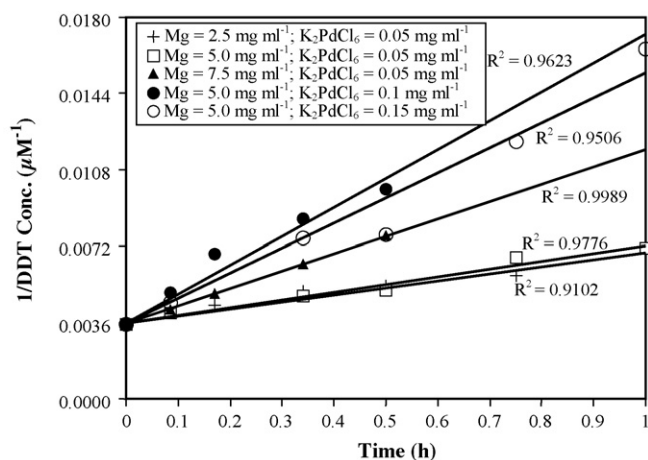
Fig. 6. Kinetic profiles for DDT dechlorination using varying concentrations (as indicated in the figure) of Mg^0–K_2PdCl_6 in water:acetone (1:1) phase in the absence of acid. Initial concentration of DDT was fixed at 281.69 μM.

of DDT and (b) three-fold enhancement in the concentration of Mg^0 (2.5–7.5 mg ml^{-1}) or K_2PdCl_6 (0.05–0.15 mg ml^{-1}) results in nearly 2–2.5-fold increase in the rate constant value. We were unable to detect any partially dechlorinated intermediates or end products like DDD, DDE, DDMS and DDMU by GC-ECD in any of the reactions conducted using Mg^0/Pd^{4+} even if the reactions were conducted for shorter time (1–10 min) using trace concentrations of the bimetallic system and at temperatures as low as 4 °C.

The GC–MS pattern following 30 min of the reaction of DDT with Mg^0/Pd^{4+} in 1:1 water:acetone revealed the presence of a dominant peak at 4.26 min (GC–MS profile not shown). The fragmentation pattern of this peak matched that of DPE thereby suggesting elimination of all the five chlorine atoms from DDT. The above results are in agreement with those obtained following treatment of DDT with Mg^0/Pd^{4+} in 0.05% biosurfactant phase thereby suggesting that substitution of water–acetone with biosurfactant does not affect the pathway of reaction. Our results support the previous observation reported by Engelmann et al. wherein DDT was dechlorinated to DPE using water–acetone phase under acidic conditions [13].

3.3. Optimization of acetone–water ratio for DDT dechlorination

The solubility of DDT in an aprotic solvent such as acetone is a critical parameter that influences the mass transfer and hence rates of dechlorination. Therefore, the effect of varying ratios of water–acetone on the extent of DDT dechlorination by Mg^0/Pd^{4+} system was examined. It may be noted from Table 2 that highest loss of DDT (86% ± 4) was obtained using 1:1 ratio while with 19:1 ratio, only 40% disappearance was observed in 4 h. Water–acetone ratios of 2:1, 4:1, and 9:1 showed 75–78% dechlorination. At lower ratio (19:1), the amount of acetone would be insufficient to dissolve entire DDT and thus limits its dechlorination. A water–acetone ratio of 9:1 in combination with biosurfactant may be optimal for large-scale destruction of DDT. Appropriate combination of small volumes of acetone

Table 2
Optimization of water–acetone ratio for DDT dechlorination

S. no.	Water:acetone (v/v)	Initial [DDT] (ppm)	Remaining [DDT] (ppm)	%Disappearance
1	1:1	50	6.8	86.4
2	2:1	50	10.8	78.4
3	4:1	50	10.5	79.0
4	9:1	50	12.35	75.3
5	19:1	50	29	42.0

Reaction mixture contained K_2PdCl_6/Mg^0 (0.1 mg/5 mg/ml). Reactions were conducted in the absence of acid and the total reaction time was 4 h.
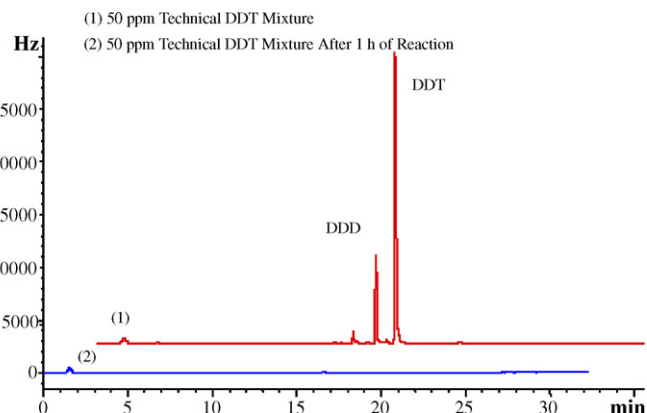

Fig. 7. Comparison of GC-ECD profiles of untreated (control) and Mg^0/Pd^{4+} (10 mg/0.2 mg ml^{-1}) treated commercial grade DDT mixture. Biosurfactant solution (0.01% in water) was used as the reaction phase and time of reaction was 1 h. Acetic acid (333 mM) was included in the reaction mixture.

with biosurfactant solution will not only reduce the cost but also be environmentally friendly.

3.4. Dechlorination of technical DDT mixture using Mg^0–Pd^{4+} system in biosurfactant phase

Technical grade DDT (50 ppm) also containing significant amounts of DDD was dechlorinated almost completely by the Mg^0/Pd^{4+} (10 mg/0.2 mg ml^{-1}) within 1 h in water–biosurfactant phase under acidic conditions (Fig. 7). Partially dechlorinated intermediates were not detected by GC-ECD. Based on this experiment we assume that Mg^0/Pd^0 catalytic reaction has the potential to dechlorinate technical grade of DDT

Table 3
Comparison of DDT dechlorination efficiency of Pd^0–alumina pellets and K_2PdCl_6

Nature of palladium	Initial [DDT] (ppm)	Remaining [DDT] (ppm)	%Disappearance
K_2PdCl_6	50	BDL[a]	>99
K_2PdCl_6	100	5.5	95
Pd^0–alumina	50	29	42
Pd^0–alumina	100	64	36

Reaction conditions: 2 ml of reaction mixture contained K_2PdCl_6/Pd^0 alumina (0.24 mg Pd elemental weight in each case), 10 mg Mg^0 and 33.3 mM acetic acid. Total reaction time was 30 min.
[a] BDL: below detection limit.

Table 4
Reuse efficiency of Pd^0–alumina (immobilized Pd) for DDT dechlorination

Reaction cycle no.	Strength of acetic acid (mM)	Total reaction time (h)	Initial [DDT] (ppm)	Remaining [DDT] (ppm)	% DDT disappearance
I (fresh reaction mix)	33.3	2	50	3.0	94
II	33.3	2	50	5.0	90
III	33.3	6	50	3.0	94
IV	333	6	50	0.2	>99
V[a]	333	6	50	16	68

First use reaction mixture (2 ml) contained 48 mg Pd^0–alumina (0.24 mg Pd), 10 mg Mg^0 and acetic acid (strength as indicated). Total reaction time for individual cycles are indicated in the table.

[a] During this cycle Mg^0 was totally dissolved.

and could be very useful under natural conditions since it leaves no partially chlorinated intermediates behind.

3.5. DDT dechlorination efficiency by Pd^0–alumina pellets in comparison to that of K_2PdCl_6 salt

Table 3 compares the extent of DDT disappearance due to dechlorination by Mg^0/Pd^0–alumina and Mg^0/Pd^{4+} systems in the presence of acid. Results reveals that within 30 min, the coordinate complex salt dechlorinates >99% of 50 ppm initial DDT and 95% of 100 ppm DDT. On the other hand, Pd^0 alumina pellets were able to dechlorinate only 42 and 36% of 50 and 100 ppm DDT, respectively. Results clearly demonstrate the superior performance of the coordinate complex salt (K_2PdCl_6) as compared to Pd^0. However, longer reaction times (2 h or more) enhanced DDT removal efficiencies by Pd^0 pellets to >90%.

3.6. Reuse efficiency of Pd^0–alumina pellets

Table 4 presents results related to reuse capacity of Mg^0/Pd^0–alumina pellets for DDT removal. Results demonstrate that magnesium as well as Pd^0–alumina pellets could be recycled for four successive reactions with DDT removal efficiencies in the range of 90–99%. Longer reaction time (6–12 h) in the first cycle resulted in total dissolution of Mg^0. Thus maintaining shorter reaction periods (2 h) in the first two catalytic cycles was crucial for the subsequent reuse. The third, fourth and fifth cycles required longer reaction time (6 h or more). The fifth reaction cycle could achieve only 70% dechlorination of DDT accompanied by total dissolution of magnesium granules after 6 h. At this stage, non-availability of Mg^0 seemed to be limiting the progress of dechlorination reaction. Morales et al. examined the potential of Pd^0–alumina in combination with magnesium and iron to hydrogenate phenol [18]. They compared the hydrogenation capacity of Pd^0 pellets in absence and presence of acid. Absence of acid slowed the hydrogenation reaction. However when acid was added, reaction was completed within 6 h with ~93% hydrogenation with total consumption of Mg^0. However Pd^0 pellets could be reused.

The reuse of Pd^0–alumina pellets may be very useful since palladium is expensive and its toxicity effects are not well known. Additionally, pellets may be used in designing reactor or reactive permeable barrier for the treatment of ground water contaminated with chlorinated organics. Furthermore, Pd^0–alumina

is a common commercially available preparation. This feature may offer rapid scale-up in order to accommodate industrial waste streams. However, cost-analysis needs to be performed.

4. Conclusions

Mg^0/Pd^0 bimetallic system was found to be efficient for dechlorinating DDT up to concentrations as high as 100 ppm within 1 h, provided the target compound is solubilized through addition of acetone or biosurfactant in the aqueous phase. The use of biosurfactant to solubilize DDT may be a better option for application to natural contaminated sites and large-scale industrial effluent treatment. GC-ECD and GC–MS analyses reveal complete dechlorination of DDT to DPE (diphenylethane) in both reaction phases with no accumulation of partially dechlorinated intermediates. Technical mixture of DDT was dechlorinated completely in aqueous phase containing biosurfactant. It was observed that presence of acid enhances the rate of reaction by providing adequate protons for the production of hydrogen and by solubilizing metal hydroxide. The cost of palladium is a major concern and in this respect reuse of Pd^0–alumina pellets may offer economic advantages over the salt form of palladium. We conclude that it may be worthwhile to evaluate Mg^0/Pd^0 reactive system for designing indigenous permeable barriers or reactors for DDT contaminated water or waste effluent. The major advantages of the proposed system are:

- higher rate of dechlorination than microbial systems;
- no accumulation of partially dechlorinated intermediates like DDD, DDE, and DDMU;
- no precaution is required to exclude oxygen in the reaction phase.

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