

Transformation of DDT and Its Metabolites by Various Abiotic Methods

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Abstract: This work looks at several new abiotic treatment methods for transformation of DDT in an aqueous solution. Various combinations of calcium peroxide (CaO₂), zero-valent iron (Fe⁰), iron sulfide (FeS), and hydrogen peroxide (H₂O₂) were utilized to promote the abiotic transformation of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) in electrolyte, hydroquinone, and nonionic surfactant (Triton X-114) systems. Treatment with CaO₂ resulted in 86% DDT mass reduction within 10 days of treatment with only traces of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE), and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (DDMU) being generated. Treatments with 1:1 mixtures of Fe⁰:CaO₂ and FeS:CaO₂ resulted in 86 and 85% DDT mass transformation, respectively, within 8 days. A mixture of 0.75 g Fe⁰:0.1 g CaO₂ showed similar results with 79% DDT mass transformed within 8 days. A mixture of 0.75–0.1 g of Fe⁰:FeS resulted in 85 and 97% transformation in the total mass of DDT in an electrolyte solution and a hydroquinone solution, respectively. The treatment of DDT in aqueous solution by CaO₂, in the presence of Triton X-114, resulted in the transformation of 97% of the total mass of DDT within 30 days, albeit, large amounts of DDE (402 μM) were generated.

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Introduction

Chlorinated pesticides such as 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) have been used for pest control in agriculture and forestry worldwide since World War II (Foreman and Gates 1997; Nowel et al. 1999). DDT was banned on agricultural soils in the United States in 1972 (Sayles et al. 1997; Nowel et al. 1999) and some parts of Europe by the late 1970s (Foght et al. 2001). Yet, high concentrations of DDT and its transformation products 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) are still found in soils and sediments in many locations throughout the country, such as the Sunflower River in Mississippi (Nowel et al. 1999). DDE and DDD exist as impurities in commercial DDT formulations (2.4 and 7.5%, respectively, mol/mol basis) as well as formed during the abiotic environmental transformation of DDT (Sayles et al. 1997; Quensen et al. 1998; Foght et al. 2001). DDT, DDD, and DDE remain contaminants of con-

cern in soils and sediments due to their low aqueous solubility (3, 40, and 160 μg L⁻¹, respectively) and high octanol-water partition coefficients (log *K*_{OW}=6.36, 5.69, and 6.02, respectively). The half-life of DDT and its metabolites depends upon soil conditions and may vary from 3 to 30 years (Dimond and Owen 1996).

Historically several abiotic methods have been explored for the transformation DDT. Hall et al. (1996) used ball milling in combination with calcium oxide (CaO) to treat DDT. Other researchers have explored the use of zero-valent iron (Fe⁰), ferric and ferrous iron (Fe⁺², Fe⁺³), and ferrous sulfide (FeS) for abiotic reductive dechlorination of DDT (Boul et al. 1994; Sayles et al. 1997; Glass 1972; Baxter 1990). More efficient means of transforming DDT, especially in a natural environment, need to be determined.

The focus of these screening level experiments was to investigate how various combinations of calcium peroxide (CaO₂), Fe⁰, FeS, and sequential additions of hydrogen peroxide (H₂O₂) could abiotically transform DDT in a 0.01 M CaCl₂ electrolyte, Triton X-114 surfactant, and hydroquinone aqueous solutions. Fe⁰ was chosen based on previous work that demonstrated that Fe⁰ and other forms of reduced iron were effective in the reductive dechlorination of DDT (Sayles et al. 1997). FeS was chosen for comparison with Fe⁰ because it is more environmentally stable than Fe⁰ and it could present a more cost-effective, naturally occurring treatment option if found to be as effective as Fe⁰ (Gander et al. 2002; Kenneke and Weber 2003). Schwarzenbach et al. (1990) stated that FeS was one of the most abundantly occurring natural reductants in anaerobic soils and sediments. Due to the difference in oxidation states of the iron in both compounds, and the presence of sulphide in FeS, it can be expected that there will be differences in the rate and extent of transformation of DDT. CaO₂ was chosen because it is more stable than H₂O₂ and peroxide has been shown to transform DDT. Combinations of FeS, Fe⁰,

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and CaO_2 were studied so that their combined effect on the transformation of DDT could be examined.

Materials and Methods

Chemicals

Electrolytic iron powder (Fe^0 , 100 mesh); iron sulfide (FeS); calcium peroxide (CaO_2); calcium chloride (CaCl_2); sodium hydroxide (NaOH); 5 hydroxy-1,4-naphthoquinone (juglone); 50% hydrogen peroxide, Triton X-114; chromatography grade hexane, acetone, toluene, and ethanol were obtained from Fisher Scientific (Fair Lawn, N.J.). DDT 98% purity; DDE 99% purity; and DDD 97% purity were obtained from Sigma (Milwaukee) and were used without further purification.

Treatment Procedures

CaO_2 and Mixed Abiotic Treatments

DDT, DDD, and DDE stock solutions (5 mM each) were prepared in chromatography grade acetone. A 0.01 M CaCl_2 solution was prepared in distilled deionized water and was used as the background electrolyte to mimic the natural soil-water environment. Glass vials (16-mL capacity) with Teflon-lined septa caps were used as reaction vials. CaO_2 (0.750 ± 0.002 g) was weighed directly into the reaction vials and 8 mL of 0.01 M CaCl_2 was added. For the mixed reaction vials, abiotic agents were added as follows: a 1:1 mixture by weight of Fe^0 : CaO_2 , FeS : CaO_2 (0.375 ± 0.002 g each) as well as 1:0.13 mixtures by weight of Fe^0 : FeS or Fe^0 : CaO_2 were explored. Reaction vials were spiked with 450 μL of DDT stock solution to achieve approximately 800 μg (500 μM) of DDT per reaction vial. The concentration of the stock was verified by gas chromatography. As this was a screening test to identify different chemical mixtures that could transform DDT in aqueous solutions, the DDT concentrations employed in this study were higher than typically found in the soil-water environment. The most effective abiotic methods will be used in future work employing environmentally relevant DDT concentrations. Reaction vials were tightly sealed with Teflon-lined screw caps to prevent any loss of solution. To ensure proper sealing, Teflon tape was applied to the threads of the reaction vials before screwing the caps on. To minimize the influence of diffusion induced by stratification in the aqueous phase or into the Teflon cap, reaction vials were mixed continuously with a rotary shaker in complete darkness. Controls without the addition of any abiotic agent were also prepared to account for possible loss of DDT due to interactions with reaction vials and caps. Sufficient numbers of reaction vials were used to allow for six reaction vials (three for control and three for treatment) to be sacrificed for each sampling time. No loss of DDT was observed in the controls. Error bars in figures represent standard deviation between the triplicate samples with a 95% confidence interval.

Hydroquinone

Hydroquinone solution was made by combining 5 hydroxy-1,4-naphthoquinone (87 ± 0.10 mg) in 100 mL of HPLC grade acetone. Hydroquinone solution (160 μg) was added to each reaction vial. Fe^0 (0.75 g) as well as a 1:0.13 mixture of Fe^0 : FeS were added to 8 mL of hydroquinone in the reaction vials and spiked with

450 μL of DDT stock solution as previously described. Samples were shaken for predetermined times (0, 4, 8, 24, 48, 96, and 192 h).

Reaction vials were removed from the shaker at specific times. Hexane (5 mL) was added to each vial and then returned to the shaker for 2 h. The vials were taken off the shaker and an aliquot from the hexane was removed for chemical analysis. The mass of DDT transformed by the abiotic treatments (reported by percent removed) was calculated from the difference in concentrations between the controls and the treatment reaction vials.

Analytical Methods

A Hewlett Packard 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and an autosampler (HP7673) was used for DDT, DDE, and DDD analyses. The GC capillary column (HP-5, 30 m \times 0.32 mm, 0.25- μm film thickness) was obtained from Agilent Technologies. Ultrahigh purity helium (flow rate of 2.5 mL min^{-1}) and nitrogen were used as the carrier and makeup gas, respectively. The sample injection volume was 3 μL splitless for samples without surfactant and the injector temperature was set to 275°C. The oven temperature was ramped from 150 to 154°C at 5°C min^{-1} and 154 to 290°C at 25°C min^{-1} (hold for 0.5 min) for nonsurfactant treatments. For samples with surfactant the method had to be changed due to the effect of the surfactant on the GC column. The injection volume was 2 μL splitless; the oven temperature was ramped from 150 to 154°C at 5°C (hold for 1 min), and 154 to 290°C (hold for 4.26 min). The detector temperature was maintained at 290°C. This method was determined experimentally for the most efficient elution of DDT and its metabolites in a hexane supernatant. Standards of DDT, DDE, and DDD (1–450 μM) were prepared by diluting the stock (5 mM) solutions in chromatography-grade acetone for constructing calibration curves, which were used to determine DDT, DDE, and DDD concentrations. Calibration samples were run every 25 samples as external standards. DDD and DDE were seen in the controls, baseline concentrations were 12 and 7 μM , respectively.

Results and Discussion

Redox Potential

Reactants for these experiments were chosen based on their potential to reduce/oxidize DDT and its metabolites and their stability in the environment (for comparisons between more stable and less stable forms). Standard electrode potentials (volts) given by Bratsch (1989) for half-reactions in water at 298.15 K were used to estimate reactions and associated by-products. E° for the following half-reactions are $\text{Fe}^{2+}/\text{Fe}(c)$, -0.44 ; Ca^{2+}/Ca , -2.868 ; $\text{Fe}^{3+}/\text{Fe}^{2+}$, 0.771 ; H_2O_2 , H^+/OH , 0.96 ; and H_2O , $\text{Sg}(c)/\text{S}^{2-}$, -0.57 . It was anticipated that CaO_2 and H_2O_2 would result in the most complete transformation of DDT and its metabolites, as the free radicals formed during transformation should scavenge everything available. Matheson and Tratnyek (1994) showed that Fe^0 has a greater redox potential and will transform faster at pH 7 than the reaction of Fe^{2+} to Fe^{3+} , suggesting that Fe^0 will result in greater transformation than FeS . Sayles et al. (1997) showed that the amount of Fe^0 and the addition of Triton X-114 had no significant effect on the redox potential of their systems, so varying the amount of metals and the addition of surfactant should not have a detrimental effect on the ability of reactants to transform

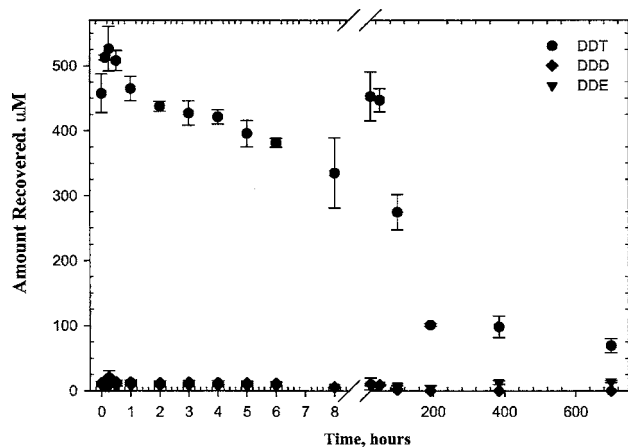


Fig. 1. Kinetics of DDT transformation by CaO_2 and production of metabolites DDD and DDE in aqueous solutions

DDT and its metabolites, although the solubility of DDT, due to the addition of surfactant, should increase the ability of the reactants to transform it.

DDT Transformation by CaO_2

To achieve near-environmental conditions, all experiments were carried out without buffering the solution pH or altering the redox conditions of the systems (i.e., by purging the reaction vials with helium or any other inert gas). Solution pH varied for various reactants remaining at approximately 11 for all CaO_2 experiments, 9.7 for all FeS and Fe^0 experiments. These values were reached within a few hours and did not fluctuate significantly throughout the duration of the experiment. The kinetics of DDT destruction by CaO_2 (Fig. 1) shows that CaCO_2 resulted in 86% of DDT transformation within 10 days of treatment. The experiment was continued for 30 days to verify completion of reaction. Fig. 1 shows the production of DDD and DDE (0 and 10 μM , respectively, within 10 days) during transformation of DDT. No DDMU was produced by transformation with CaO_2 . The amounts of DDD and DDE accumulated in the CaO_2 reaction vials were not significantly above the background levels. These observations suggest that DDT may have been tightly bound to the CaO_2 surface, transformed into polar compounds that were not extracted by hexane or mineralized into CO_2 . Due to the redox potential of CaO_2 , transformation to polar compounds is a viable possibility. Possible sorption of DDT to the CaO_2 surface could also account for the large error bars seen on some triplicate samples (Figs. 1 and 2), especially for the shorter treatment times where the system may not have had time to equilibrate. Additional work is needed to determine the pathway of DDT transformation by CaO_2 .

Small peaks in addition to DDE, DDD, and DMU were also observed on some of the GC chromatograms for longer treatment times. This may indicate that other transformation products of DDT could be forming, but the areas of those peaks were insignificant, therefore no attempt was made to identify and quantify those compounds. Only about 5% of the total DDT mass lost during the treatment time was recovered as DDD and DDE.

To ensure that solubility of DDT was not a limiting factor in transformation via CaO_2 , the above experiments were run in a 0.13 mM Triton X-114 solution. Weber (1996) had observed that use of zero-valent iron treatment for contaminants such as DDT

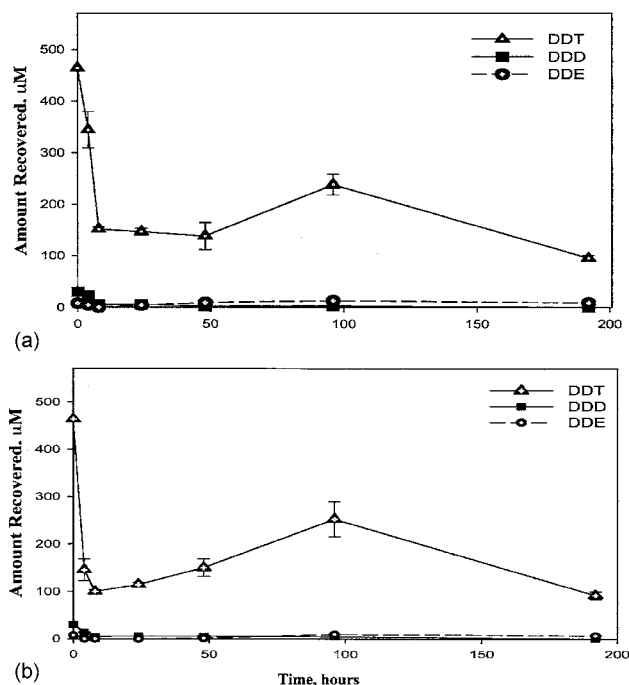


Fig. 2. (a) Kinetics of DDT transformation by $\text{CaO}_2:\text{Fe}^0$ and production of metabolites DDD and DDE. (b) Kinetics of DDT transformation by $\text{CaO}_2:\text{FeS}$ and production of metabolites DDD and DDE.

that are strongly sorbed to natural surfaces might not be feasible. Exploration of surfactant use for iron and CaO_2 is expected to overcome the availability issue. It has been shown previously that nonionic surfactants such as the Triton series can enhance the solubility of DDT, even below the critical micelle concentration (CMC) (0.2 mM for Triton X-114) (Kile and Chiou 1989). After 16 days, only 61% of the added DDT mass was transformed. However, those samples run for 30 days showed a 97% reduction in the added DDT mass. Within the reaction vials run for 30 days, a large buildup of DDE was observed with only minor amounts of DDD (402 and 48 μM). There was no significant buildup of DDE in any other experimental systems. While the near-complete transformation of DDT in these reaction vials was encouraging, the buildup of DDE may be problematic since DDE has been shown to be more persistent than DDT (Boul et al. 1994).

DDT Transformation by a Mixture of Abiotic Agents

DDT transformation by 1:1 (w/w) mixtures of $\text{CaO}_2:\text{Fe}^0$ and $\text{CaO}_2:\text{FeS}$ was investigated. Figs. 2(a and b) show that the mixtures of abiotic agents transformed DDT within aqueous solutions more effectively than individual abiotic agents with 85% of the original DDT mass transformed within 8 days in both systems. DDD and DDE were not observed above baseline concentrations when $\text{Fe}^0:\text{CaO}_2$ and $\text{FeS}:\text{CaO}_2$ mixtures were used to transform DDT. This was perhaps due to the more complete transformation of DDT (to polar compounds) by CaO_2 or due to sorption on the CaO_2 surface.

Non 1:1 mixtures were also used to see what effect varying the available reaction surface area would have on the transformation kinetics of DDT. Fe^0 (0.75 g) was combined with 0.1 g of either CaO_2 [Fig. 3(a)] or FeS [Fig. 3(b)] and samples were run as detailed above. In the $\text{Fe}^0:\text{CaO}_2$ system [Fig. 3(a)], a 79% trans-

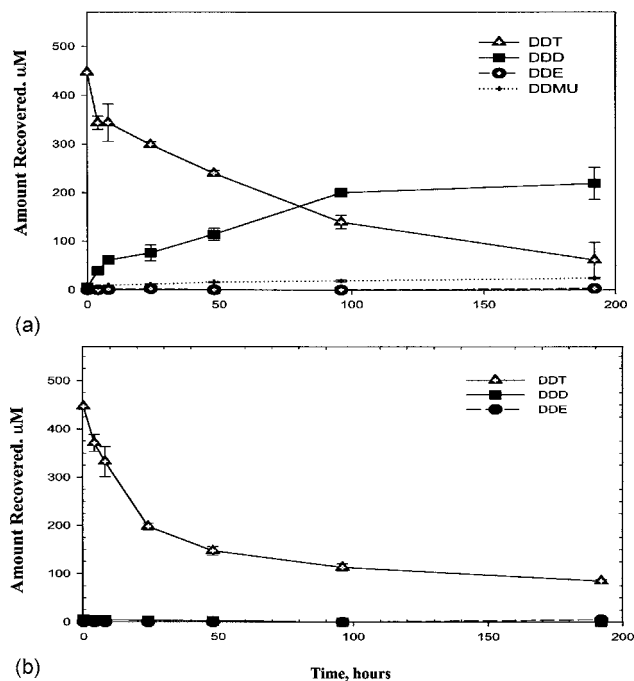


Fig. 3. (a) Kinetics of DDT transformation by a 1:0.13 mixture of Fe⁰:FeS and production of metabolites DDD, DDE, and DDMU. (b) Kinetics of DDT transformation by a 1:0.13 mixture of Fe⁰:CaO₂ and production of metabolites DDD and DDE.

formation of DDT mass was observed with no significant production of transformation metabolites after 8 days. In the Fe⁰:CaO₂ system, 20% of the added DDT mass was recovered as DDT or its metabolites. In the Fe⁰:FeS systems [Fig. 3(b)], an 85% reduction in the mass of DDT was observed within 8 days of treatment, with production of 221 μM DDD and 23 μM DDMU, respectively. In the Fe⁰:FeS system, 67% of the added DDT was retrieved as DDT or its metabolites.

DDT Transformation by Mixed Abiotic Agents in the Presence of H₂O₂

Sequential reduction and oxidation using Fe⁰ and H₂O₂ has been shown to enhance abiotic transformation of nitroaromatic compounds (Hundal et al. 1997). To determine if similar results could be obtained with DDT, H₂O₂ was used in combination with a 1:0.13 (w/w) mixture of Fe⁰:FeS. The abiotic transformation of DDT was evaluated by adding 1 mL of 50% H₂O₂ at either the beginning of the reaction or halfway through the predetermined experiment duration (Fig. 4). When H₂O₂ was added to the reaction vials initially [Fig. 4(a)], a 95% transformation in the mass of DDT was observed after 4 days of treatment. Only moderate production of DDD and DDMU (118 and 38 μM, respectively) was observed. DDE production was insignificant (5 μM). When H₂O₂ was added after half of the experimental time had elapsed [Fig. 4(b)], an 89% transformation of the total mass of DDT was observed with moderate amounts of DDD and DDMU (91 and 30 μM) present in the system. There was no significant production of DDE after 4 days of treatment.

DDT Transformation in Hydroquinone Solution

Electron transfer from the metal surface to the contaminant surface drives DDT transformation by Fe⁰ (Matheson and Tratnyek

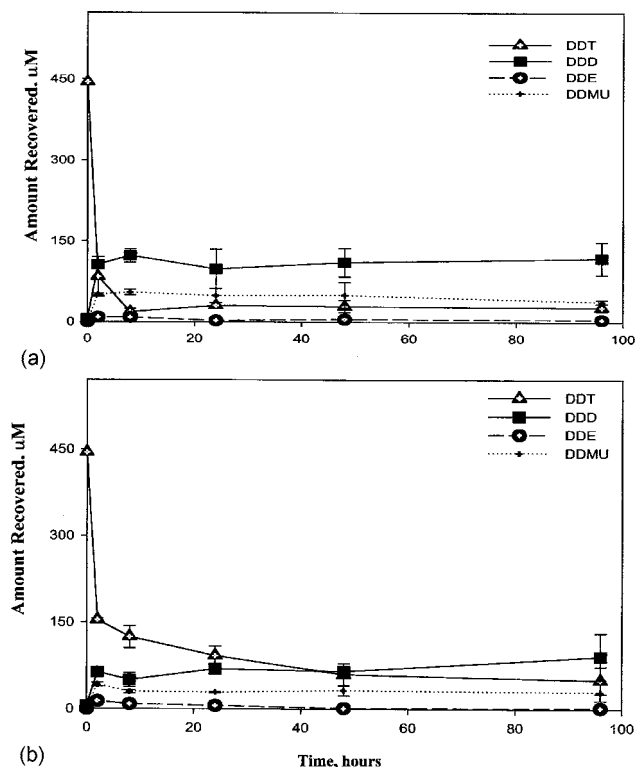


Fig. 4. (a) Kinetics of DDT transformation by a 1:0.13 mixture of Fe⁰:FeS with sequential additions of H₂O₂ when added initially to reaction vials and production of metabolites DDD, DDE, and DDMU. (b) Kinetics of DDT transformation by a 1:0.13 mixture of Fe⁰:FeS with sequential additions of H₂O₂ when added after half of the treatment time had elapsed and production of metabolites DDD, DDE, and DDMU.

1994). Therefore a hydroquinone solution should facilitate electron transfer between Fe⁰ and the contaminant surface, much as quinone functional groups do in natural organic matter (Schwarzenbach et al. 1990; Dunnivant et al. 1992; Perlinger et al. 1996; Tratnyek et al. 2001). In sediments, quinones are reduced by HS⁻ and produce hydroquinones, which may assist in reducing halogenated compounds (Perlinger et al. 1996). To study the effect of hydroquinone on the transformation of DDT, 160 μL of 100 μM hydroquinone was added to the Fe⁰-DDT systems. An 80% transformation of DDT was seen in 4 days. The enhancement in transformation rates could be contributed to the enhanced ability of the system to transfer electrons with the hydroquinone acting as an electron mediator. Transformation with mixtures of abiotic agents in combination with the hydroquinone solution was carried out using a mixture of 0.75 g Fe⁰ and 0.1 g FeS. This system was run for 8 days and a 97% transformation of the DDT mass was observed (Fig. 5). Significant amounts of DDD were present, although the amount of DDMU and DDE present in the system were not above background levels (198, 21, and 8 μM, respectively).

Conclusions

These results show that DDT can be transformed abiotically using several different abiotic methods. Treatment of DDT with CaO₂ alone resulted in an 86% DDT mass reduction within 10 days of treatment and DDT degradation products such as DDD, DDMU,

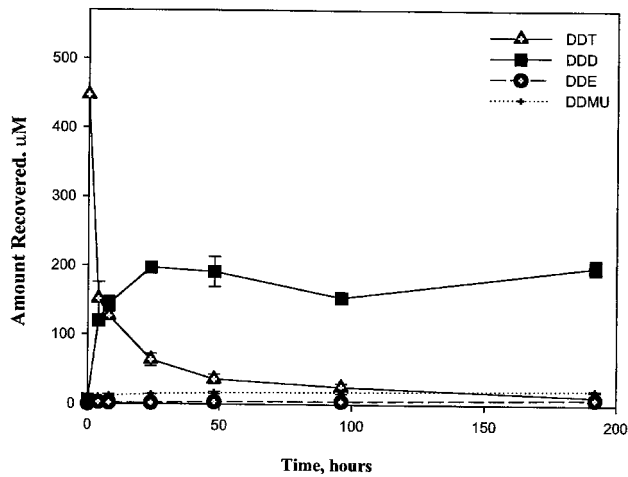


Fig. 5. Kinetics of DDT transformation by a 1:0.13 mixture of Fe^0 : FeS in a hydroquinone solution and production of metabolites DDD, DDE, and DDMU

and DDE were not generated as the concentrations of these compounds did not exceed the background levels even after 30 days of treatment. Treatment with 1:1 mixtures of Fe^0 : CaO_2 and FeS : CaO_2 resulted a DDT mass reduction of 86 and 85%, respectively, within 8 days of treatment. A mixture of 0.75 g Fe^0 :0.1 g CaO_2 resulted in a 79% transformation within 8 days. In addition, within 8 days of treatment, a mixture of 0.75–0.1 g of Fe^0 : FeS resulted in 85 and 97% transformation of DDT in an electrolyte solution and a hydroquinone solution, respectively. The transformation of DDT in aqueous solution by CaO_2 in the presence of Triton X-114 resulted in a 97% transformation of DDT within 30 days with a build-up of a significant amount of DDE (402 μM). The loss of DDT mass in these systems must be explored further. Treatments that only accomplished 79–90% transformation of DDT in systems that contained no sorbing material (such as soils or sediments) are not recommended for treating natural systems. These compounds do show promise in transforming DDT, but other mixtures or combinations need to be explored to find more efficient and effective means of treatment.

Hydroquinones are very effective electron mediators and can be used to model naturally occurring electron mediators in the environment. Addition of hydroquinones in our experiments has been shown to accelerate the rate of DDT transformation in aqueous solution. The use of natural hydroquinones (natural organic matter or humics) should be explored to enhance the efficiency of abiotic treatments of DDT in the environment. The surface area of the abiotic agents does not appear to have a significant effect on the kinetics of DDT transformation.

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